Novel SF$_5$- and CF$_3$-containing organyls

by

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Doctor of Philosophy in Chemistry

Approved Dissertation Committee

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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>AcOH</td>
<td>Acetic acid</td>
</tr>
<tr>
<td>AM LCD</td>
<td>Active Matrix Liquid Crystal Display</td>
</tr>
<tr>
<td>Ar</td>
<td>Aryl</td>
</tr>
<tr>
<td>aq</td>
<td>Aqueous</td>
</tr>
<tr>
<td>ax</td>
<td>axial</td>
</tr>
<tr>
<td>BuLi</td>
<td>Butyl lithium</td>
</tr>
<tr>
<td>d</td>
<td>Doublet</td>
</tr>
<tr>
<td>d</td>
<td>day</td>
</tr>
<tr>
<td>DBU</td>
<td>1,8-Diazabicyclo[5.4.0]undec-7-ene</td>
</tr>
<tr>
<td>DDQ</td>
<td>2,3-Dichlor-5,6-dicyano-1,4-benzochinone</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N'-Dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>Et</td>
<td>Ethyl</td>
</tr>
<tr>
<td>eq</td>
<td>Equivalent</td>
</tr>
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<td>eq</td>
<td>equatorial</td>
</tr>
<tr>
<td>g</td>
<td>Grams</td>
</tr>
<tr>
<td>GABA</td>
<td>y- aminobutyric acid</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>HMDS</td>
<td>Hexamethyldisiloxane</td>
</tr>
<tr>
<td>HRMS</td>
<td>High Resolution Mass Spectrometry</td>
</tr>
<tr>
<td>hν</td>
<td>Energy E of a photon</td>
</tr>
<tr>
<td>J</td>
<td>Coupling constant</td>
</tr>
<tr>
<td>KHMDS</td>
<td>Potassium bis(trimethylsilyl)amide</td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Crystal</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid Crystal Display</td>
</tr>
<tr>
<td>LHMDS</td>
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</tr>
<tr>
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<tr>
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<td>Acetonitrile</td>
</tr>
<tr>
<td>Me</td>
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</tr>
<tr>
<td>min</td>
<td>Minute</td>
</tr>
<tr>
<td>MHz</td>
<td>Mega Hertz</td>
</tr>
<tr>
<td>mL</td>
<td>Millilitre</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>Symbol</td>
<td>Term</td>
</tr>
<tr>
<td>---------</td>
<td>---------------------</td>
</tr>
<tr>
<td>o</td>
<td>ortho</td>
</tr>
<tr>
<td>p</td>
<td>para</td>
</tr>
<tr>
<td>Ph</td>
<td>Phenyl</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>r. t.</td>
<td>room temperature</td>
</tr>
<tr>
<td>s</td>
<td>Singlet</td>
</tr>
<tr>
<td>t</td>
<td>Triplet</td>
</tr>
<tr>
<td>TFA</td>
<td>Trifluoroacetic acid</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>t-BuOK</td>
<td>Potassium-tert-butoxide</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>quin</td>
<td>Quintet</td>
</tr>
<tr>
<td>quart</td>
<td>Quartet</td>
</tr>
<tr>
<td>δ</td>
<td>Density</td>
</tr>
<tr>
<td>μ</td>
<td>Molecular dipole moment</td>
</tr>
<tr>
<td>Δε</td>
<td>Dielectric anisotropy</td>
</tr>
<tr>
<td>Δn</td>
<td>Birefringence</td>
</tr>
<tr>
<td>°C</td>
<td>Degree Celsius</td>
</tr>
<tr>
<td>δₚ</td>
<td>Hammet substituent constant</td>
</tr>
<tr>
<td>P</td>
<td>Hantzsche hydrophobicity constants</td>
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Abstract

The limitation of pentafluoro-$\lambda^6$-sulfanyl (SF$_5$) sources and building blocks stimulates great interest for investigating new approaches for synthesizing of SF$_5$-containing compounds. The properties of the SF$_5$-group often are compared with those of the CF$_3$-group and the “advantages” of the SF$_5$-group were hence referred to as a “super CF$_3$-function”.

In this work, new synthetic routes towards SF$_5$ and CF$_3$ containing aromatics are presented. The first route is the radical addition of SF$_5$Cl and CF$_3$I to double bonds of 7-oxabicyclo[2.2.1]hept-2-ene derivatives, the second approach shows an improved method for the synthesis and followed by fluorination of arylsulfur chlorotetrafluorides to give arylsulfur pentafluorides. Key steps of the synthetic sequence for the first approach were based upon radical addition reactions of SF$_5$Cl or CF$_3$I as sources of SF$_5$- and CF$_3$-groups, to the double bond of different 7-oxabicyclo[2.2.1]hept-2-ene derivatives. Dehydrohalogenation followed by aromatization leads to pentafluorosulfanyl and trifluoromethyl aromatics, respectively.

The second synthetic route is the fluorination of arylsulfur chlorotetrafluorides to yield arylsulfur pentafluorides. Treatment of different aryl thiols and diaryl disulfides with chlorine and potassium fluoride provides the corresponding arylsulfur chlorotetrafluorides. The application of new conditions using KHF$_2$ and TFA converts these compounds to arylsulfur pentafluorides.
Theoretical Background

A Theoretical Background

A.1 Introduction

The introduction of fluorine into organic compounds has been observed to have unique effects.\[^{1}\] Perfluoroalkanes, especially, can assume a purely physical function, for example oxygen transport, but are foreign to the living system to such an extent that they are not recognized and are completely ignored by the body.\[^{2}\]

One of the most common fluorine containing substituents is the CF\(_3\)-group.\[^{2}\]

Many different CF\(_3\)-containing compounds have been synthesized and used in different fields,\[^{2-3}\] but in the last 10 years investigations have started to focus more and more on a less known, but also biologically active and possibly more effective substituent; the SF\(_5\)-group ("super CF\(_3\)-group").\[^{2}\] The introduction of a pentafluoro-\(\lambda^6\)-sulfanyl-group into organic compounds has a variety of effects on the physical and chemical properties of such compounds.\[^{2-3}\] Because of their relatively low surface energy, high chemical resistance, thermal stability, high electronegativity and lipophilicity, these compounds can also have greater biological activity relative to the CF\(_3\)-derivatives. Compared to the CF\(_3\)-group, the pentafluorosulfanyl group is much more electronegative (\(\delta_p\)(CF\(_3\)) = +0,53; \(\delta_p\)(SF\(_5\)) = +0,68) and has a higher lipophilicity (Hantzsch hydrophobicity constants, P(CF\(_3\)) = 1.09, P(SF\(_5\)) = 1.51).\[^{4-5}\] In addition, the SF\(_5\)-group has a higher thermal and chemical stability than its carbon analogue.\[^{4-5}\] SF\(_5\)-containing compounds already find application in many different fields.\[^{6-8}\]

Although the introduction of a pentafluoro-\(\lambda^6\)-sulfanyl-group into organic compounds has already been known for the past 50 years, the number of SF\(_5\)-containing compounds is limited by the availability of building blocks and SF\(_5\) sources.\[^{9}\]
A.2 Useful known SF₅-compounds

The importance of SF₅-containing organic compounds is constantly growing, as many of them have found applications in a variety of different research areas such as agriculture\textsuperscript{[10-11]} and pharmacy.\textsuperscript{[12-16]} The pentafluoro-\(\lambda^6\)-sulfanyl-group is also used in compounds for liquid crystals,\textsuperscript{[17-21]} energetic materials and explosives,\textsuperscript{[21-24]} refrigerant fluids,\textsuperscript{[21]} ionic liquids,\textsuperscript{[21]} and in polymer research.\textsuperscript{[21]} Solvents, surfactants and rocket fuels can benefit from the introduction of an SF₅-group.\textsuperscript{[6-8]} Its versatility and unique properties makes the SF₅-group one of the most interesting substituents in fluorine chemistry. Some of its known compounds and possible applications are detailed in this chapter.

In the field of agricultural chemicals, the SF₅-group has already proven its usefulness. A number of patents described the behavior of such derivatives as fungicides, herbicides and insecticides.\textsuperscript{[2-3]} The compound Fipronil \textit{Ia} is a highly effective pesticide, which blocks GABA-gated chloride channels.\textsuperscript{[10]} It shows an excellent activity against a variety of pests, including arthropods and helminthes. This SF₅-analogue is even more biologically active than Fipronil \textit{Ib} itself.\textsuperscript{[10]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{SF₅-analogue of Fipronil \textit{Ia}, Fipronil \textit{Ib}}
\end{figure}
The theoretical background discusses the use of sulfur pentafluoride and trifluoromethyl analogues in insecticidal and pharmaceutical applications. The sulfurs pentafluoride and trifluoromethyl analogue were screened against susceptible and resistant strains of houseflies and susceptible cockroaches. \( \text{Ia} \) showed more activity than the trifluoromethyl derivative, and also displayed no loss of potency towards the resistant strain of the housefly in contrast to \( \text{Ib} \) (Table 1).

<table>
<thead>
<tr>
<th>SF5-Analogue</th>
<th>Musca (S)(^a)</th>
<th>Musca (R)(^a)</th>
<th>Blatella (S)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ia} )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( \text{Ib} )</td>
<td>0.1</td>
<td>0.1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

(R)\(^a\) indicates a strain resistant to dieldrin and (S)\(^a\) is a susceptible strain.\(^{[10]}\)

Another highly effective agricultural or horticultural SF\(_5\)-containg insecticide is the phthalamide derivative \( \text{II} \) shown in Figure 2. It has an excellent insecticidal effect even when the active-ingredient is used in small amount.\(^{[11]}\)

![Figure 2: Structure of insecticide II.](image)

Besides agricultural uses, SF\(_5\)-containing compound are also very effective as pharmaceuticals. Different examples show their implementation for preventing infarcts\(^{[12]}\) or as inhibitors for different enzymes or receptors.\(^{[13-14]}\) Even SF\(_5\)-compounds with anti-cancer activities are known.\(^{[15-16]}\) The SF\(_5\)-substituent shows growing future perspective in this research area.
The unique properties of the pentafluoro-λ⁶-sulfanyl-group are of special interest for the production of liquid crystals. The most common LCDs (Liquid Crystal Displays) are based on twisted-nematic cells. The power usage is affected by the voltage response, which is determined by the dielectric anisotropy (Δε). Therefore, in order to achieve a better power usage, it is necessary to improve the dielectric anisotropy. Another important property of liquid crystals is the birefringence (Δn). A good LC material must have a very low birefringence. A polarizing head group can improve the dielectric anisotropy. Δε correlates with the molecular dipole of the compound (Figure 3).[17]

\[
\begin{align*}
\text{III a: } & X= \text{CF}_3 & \Delta \varepsilon = 8,6 \\
\text{III b: } & X= \text{CN} & \Delta \varepsilon = 21,1 \\
\text{III c: } & X= \text{SF}_5 & \Delta \varepsilon = 12,0
\end{align*}
\]

Figure 3: Dielectric anisotropy of different polarizing head groups[18-20].

The limit for active matrix liquid crystal displays (AM-LCDs) is achieved with the CF₃-group IIIa. Although the cyano-substituted LC IIIb has a much higher dielectric anisotropy, it is not usable for LCDs, because it tends to solvate ionic impurities resulting in a low voltage holding ratio, observable flicker and contrast loss in the display panel.[17] The SF₅-LC IIIc has a high dielectric anisotropy and has no tendency of solvating ionic impurities.
In addition, SF₅-LCs are even more stable against hydrolytic agents even at high temperatures compared to the CF₃-analogues and show a very low birefringence. Comparing CF₃-containing liquid crystal compounds to their SF₅-containing analogues, it is observed that using SF₅ causes a huge enhancement of the properties that are necessary for useful liquid crystal materials (Table 2).

Table 2: Dielectric anisotropy (Δε) and birefringence (Δn) of different liquid crystals.[18]

<table>
<thead>
<tr>
<th>Structure</th>
<th>dielectric anisotropy (Δε)</th>
<th>birefringence (Δn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃</td>
<td>6.8</td>
<td>0.0594</td>
</tr>
<tr>
<td>C₅H₁₁CF₃</td>
<td>7.9</td>
<td>0.0710</td>
</tr>
<tr>
<td>SF₅</td>
<td>10.5</td>
<td>0.0704</td>
</tr>
<tr>
<td>SF₅</td>
<td>10.1</td>
<td>0.0641</td>
</tr>
<tr>
<td>SF₅</td>
<td>10.4</td>
<td>0.084</td>
</tr>
<tr>
<td>C₅H₁₁SF₅</td>
<td>14.5</td>
<td>0.131</td>
</tr>
<tr>
<td>SF₅</td>
<td>15.5</td>
<td>0.134</td>
</tr>
</tbody>
</table>
The combination of this higher dielectric anisotropy, the low birefringence, the stability of SF$_5$ and the lipophilicity of the respective derivatives makes it an excellent choice towards liquid crystal material.$^{[18-19, 25]}$

Figure 5 shows the crystal structure of a pentafluorosulfanyl vinyl substituted liquid crystal IV. The C–S–F-angle is with ca. 91.48° larger than the 90° found for the basic system SF$_6$. Therefore, the equatorial fluorine atoms are along with the axial fluorine, contributing significantly to the molecular dipole moment ($\mu$) and also to the dielectric anisotropy ($\Delta \varepsilon$) of the liquid crystal.$^{[17, 19-20, 25]}$

![Crystal structure of pentafluorosulfanyl vinyl substituted liquid crystal IV](image)

Figure 5: Crystal structure of a pentafluorosulfanyl vinyl substituted liquid crystal 7.$^{[19]}$

Using SF$_5$-containing energetic materials for explosives and rocket fuels can improve their safety and effectiveness.$^{[21]}$

The SF$_5$ group has a high density compared to CF$_3$ and NO$_2$ ($\delta$ (SF$_5$) = 2.57 g/cm$^3$, $\delta$ (CF$_3$) = 2.25 g/cm$^3$, $\delta$ (NO$_2$) = 2.17 g/cm$^3$)$^{[22-23]}$ resulting in a significant improvement of the detonation pressure.$^{[21]}$ Another useful property
is the low bond energy of the S-F bond (79 kcal/mol) compared to the bond energy of the C-F bond (107 kcal/mol). For weapon systems with metallized compositions of aluminum, the conversion of S-F to Al-F (bond energy Al-F=158 kcal/mol) would be more exothermic than a similar conversion of C-F to Al-F. Therefore, SF₅ explosives are expected to be more energetic than their CF₃ analogue.[²²-²³]

2-Polynitroalkyl-5-pentafluorosulfanylperfluoroalkyl-1,3,4-oxadiazole V was found to be a new energetic plasticizer for a plastic bonded explosive, which does not migrate in fluoropolymers/nitroexplosives on storage.[²⁴]

![Image](image1.png)
**Figure 6: 2-Polynitroalkyl-5-pentafluorosulfanylperfluoroalkyl-1,3,4-oxadiazole 8.**

In order to achieve maximum energy release at the detonation it is important to prevent highly stable detonation products, such as CF₄, SF₆, or SF₄. The explosive VI has an energy release of 1065-1105 cal/g, with only hydrofluoric acid detected as a fluorine-containing detonation product.

![Image](image2.png)
**Figure 7: Structure of explosive VI.**

In 2007, Ye et al. developed a simple method of synthesizing effective explosives by “click chemistry”. [²²-²³]
Scheme 1: “Click chemistry” by Ye et al.[22-23]
A.3 SF₅-sources

The number of SF₅-containing organic compounds is limited by the availability of building blocks and SF₅ sources. Two main synthetic strategies, from recent reports, are of particular interest. The first is the radical addition of SF₅Cl and SF₅Br to double and triple bonds. A second approach is the synthesis of SF₅-containing compounds from thiols and disulfides via an arylsulfur chlorotetrafluoride. In this chapter both strategies are presented and compared to previous methods for the preparation of SF₅-containing organic compounds.

The preparation of SF₅Cl is known since 1966. Nyman, Roberts and Seaton discovered a method that converted SF₄ and CIF at 375°C under pressure (Scheme 2).[26]

\[
\text{SF}_4 + \text{CIF} \xrightarrow{375^\circ \text{C, pressure}} \text{SF}_5\text{Cl}
\]

Scheme 2: Preparation of SF₅Cl by F. Nyman, H.L. Roberts and T. Seaton.

Another preparation method has been developed in the laboratory of Schack, Wilson and Warner.[27] For further improvement, they added activated CsF to the method of Nyman, Roberts and Seaton. This reaction was carried out at ambient temperature under pressure (Scheme 3).

\[
\text{SF}_4 + \text{CIF} + \text{CsF} \xrightarrow{\text{r.t., pressure}} \text{SF}_5\text{Cl}
\]

Scheme 3: Preparation of SF₅Cl by C.J. Schack, R.D. Wilson and M.G. Warner.

Jonethal, Kuschel and Seppelt found another interesting method for the synthesis of SF₅Cl in 1988.[28] They used SF₄, Cl₂ and KF as starting compounds. All three compounds are commercially available and comparably
cheap. This reaction runs almost quantitative under certain conditions. KF has
to be dry and carefully powdered. The reaction mixture has to be agitated and
kept liquid throughout the reaction time. This can be achieved at a reaction
temperature of 75-150°C. The reaction takes several days under pressure to
be finished. The yield of this reaction is 90% (Scheme 4).

\[
\text{SF}_4 + \text{KF} + \text{Cl}_2 \xrightarrow{75-150^\circ C, \text{pressure}} \text{SF}_5\text{Cl}
\]

**Scheme 4: Preparation of SF₅Cl by U. Jonethal, R. Kuschel and K. Seppelt.**

The preparation of SF₅Br was first done by Merrill in 1962.[²⁹] SF₄ was reacted
with Br₂ and BrF₅ at 100°C under pressure. However the reaction leads to
only a small amount of product (Scheme 5).

\[
\text{SF}_4 + \text{Br}_2 + \text{BrF}_5 \xrightarrow{100^\circ C, \text{pressure}} \text{SF}_5\text{Br}
\]

**Scheme 5: Preparation of SF₅Br by C. Merrill.**

In 1965 Cohen and MacDiarmid found a method involving S₂F₁₀ and Br₂ to
prepare SF₅Br.[³⁰] The reaction temperature was 138°C (Scheme 6).

\[
\text{S}_2\text{F}_{10} + \text{Br}_2 \xrightarrow{138^\circ C} \text{SF}_5\text{Br}
\]

**Scheme 6: Preparation of SF₅Br by B. Cohen and A. MacDiarmid.**

Wessel, Kleemann and Seppelt published in 1983 a synthetic method that
used SF₄, BrF and CsF as precursors.[³¹] BrF was prepared *in situ* from
freshly distilled Br₂ and BrF₃ agitated for 14 d at ambient temperature. SF₄,
BrF and CsF were then reacted at 90°C for 15 h to give the product in 36% yield (Scheme 7).
Theoretical Background

Br₂ + BF₃

↓ r.t., 14d

SF₄ + BrF + CsF $\xrightarrow{138^\circ C}$ SF₅Br

Scheme 7: Preparation of SF₅Br by J. Wessel, G. Kleemann and K. Seppelt.

This method was optimized in 1998 by Winter, Terjeson and Gard. Here BrF is also prepared in situ from Br₂ and BrF₃ at ambient temperature in 6 to 11 d. The reaction of SF₄, BrF and CsF was also carried out at room temperature for 36 d, leading to a total yield of 99% (Scheme 8).

Br₂ + BF₃

↓ r.t., 7-11d

SF₄ + BrF + CsF $\xrightarrow{\text{r.t., 36d \ 99\%}}$ SF₅Br

Scheme 8: Preparation of SF₅Br by R. Winter, R.J. Terjeson and G. L. Gard.

A.3.1 Radical Addition of SF₅Cl to double and triple bonds

Radical addition of SF₅Cl to unsaturated olefins is an important and convenient method for the addition of a SF₅-group into organic molecules. The initiation of the radical addition has been achieved in three main routes: thermal initiation, UV-irradiation or BE₃ as a low-temperature initiator. The addition of SF₅Cl to unsaturated olefins is regio-selective, SF₅ always adds to the terminal side of the double bond.

In 1961, Case, Ray, and Roberts established thermolysis as an initiation and found that SF₅Cl adds to the double bond of unsaturated olefins like ethylenes, propenes, cyclohexenes, butadienes and vinyl chlorides when heated under high pressure (Scheme 9).
The reaction with isobutene and styrene failed as the olefins polymerized rapidly and also ethylene and vinyl chloride showed the tendency to polymerize at higher temperatures. Scheme 10 shows the formation of the side product of CIF addition. This suggests that ionic processes are taking place, which easily lead to polymerization.

Although, the radical addition of SF$_5$Br is much easier to achieve under the conditions used by Case et al., the addition of SF$_5$Cl leads to the product in almost the same yields (Scheme 11).\textsuperscript{[40-41]}

UV irradiation allows the addition of SF$_5$Cl to cyclic olefins and others without any by-products of CIF addition. Klauck und Seppelt used this method in 1994 to add SF$_5$Cl to norbornene.\textsuperscript{[35]} Irradiation of a mixture of norbornene in trichlorofluoromethane with an excess of SF$_5$Cl led to the addition product with a 98% yield (Scheme 12).\textsuperscript{[35]}
Theoretical Background

Scheme 12: Radical addition by A. Klauck und K. Seppelt.

In 2005, Brel applied this method to the SF$_5$Cl addition to alcohols.$^{[37]}$ The addition products were used to synthesize carbonyl compounds, which found application in Diels-Alder and other reactions (Scheme 13).

Scheme 13: Radical addition by Brel.

The use of BEt$_3$ as initiator allows addition reactions at low temperatures with up to quantitative yields.$^{[38-39]}$

Several different initiators are used to catalyze radical additions; triethylborane has been recognized for more than a decade to be a unique low-temperature initiator of free radical reactions.$^{[42]}$ In the case of the radical addition of SF$_5$Cl to double and triple bonds, triethylborane has been found to successfully initiate the addition reactions. The addition reactions of SF$_5$Cl are highly diastereo-selective, with essentially one product being formed from the additions to cyclohexene, trans-4-octene, and different terminal alkynes.

Scheme 14 shows the operation mode of triethylborane.$^{[43]}$ The ethyl radical reacts with SF$_5$Cl to form a very electrophilic SF$_5$ radical, which attacks the double bond of the olefin.
The reaction is carried out at low temperatures. SF$_5$Cl has a boiling point of -21°C and can easily be condensed into hexane or dichloromethane, containing the alkene or alkyne at -40°C. The BEt$_3$ initiator is added at about -30°C. The reaction time and the needed excess of SF$_5$Cl depend on the nature of the alkene or alkyne.

The usage of BEt$_3$ allows convenient addition of SF$_5$Cl to a large variety of alkenes and alkynes in excellent yields.$^{[42]}$

The addition products can lead to a variety of interesting SF$_5$-containing compounds.

The first step to utilize a SF$_5$Cl addition product is the elimination of HCl. Common methods using high temperatures or very strong bases like EtO$^-$/EtOH, OH$^-$/EtOH, NaH or BuLi can lead to the decomposition of the SF$_5$ group.$^{[38-39]}$ Different methods with moderate conditions have been established to remove HCl from the SF$_5$Cl addition product. The most common method to eliminate HCl is the usage of KOH in a mixture of water.
and ethanol, in ether or in other solvents,[34] but in most cases the reaction time is more than a week. Refluxing with \( \text{K}_2\text{CO}_3 \) in water or DMF also leads to the elimination of HCl in good yields,[7, 44] Another method uses \( \text{LiOH} \cdot \text{H}_2\text{O} \) in DMSO at room temperature.[38-39] The effectiveness of reactants for HCl elimination from \( \text{SF}_5 \)-containing compounds depends on the compound itself and is still under discussion.

Unsaturated pentafluorosulfanyl compounds are precursors for new types of dienophiles for Diels-Alder reactions.[45] Brel successfully synthesized such acids and ketones as dienophiles and reacted them with aliphatic and cyclic electron-releasing dienes to form Diels-Alder cycloadducts (Scheme 16).[45]

Radical addition of \( \text{SF}_5\text{Cl} \) has been used to form building blocks for the synthesis of \( \text{SF}_5 \)-containing heterocycles.[38-39] The addition to 7-oxa norbornene derivatives can give \( \text{SF}_5 \)-containing furans[38-39] as shown in Scheme 17.
An alternative synthetic approach towards the synthesis of SF$_5$-containing furans uses Diels-Alder/retro-Diels-Alder reaction via heating an SF$_5$ acetylene compound with 4-phenyloxazole (Scheme 18).\[38-39\]

Dolbier et al. prepared SF$_5$-containing acetylenes to synthesize SF$_5$-containing heterocycles (Scheme 19). Radical addition was followed by HCl elimination with LiOH.\[38-39\]

These acetylenes were reacted with aziridine esters to give SF$_5$-pyrrolines that could be oxidized with DDQ to the corresponding SF$_5$-pyrrols. The t-butyl
group was removed by treatment with catalytic quantities of triflic acid in dichloromethane (Scheme 20).\[^{38-39, 46}\]

![Scheme 20: Preparation of SF$_5$-pyrrols.](image)

In order to prepare SF$_5$-containing naphthalenes, radical addition to benzobarrelene was carried out. 3,6-bis-(2-pyridyl)-1,2,4,5-tetrazine was used for the aromatization step (Scheme 21).

![Scheme 21: Preparation of SF$_5$-containing naphthalenes by addition of SF$_5$Cl to double bonds.](image)

Radical addition of SF$_5$Cl to triple bonds has been carried out under similar conditions towards the addition to double bonds using BEt$_3$. The addition reaction to phenyl acetylene gives a side product of homoaddition with 27% yield, but furnishes the expected product with a 49% yield (Scheme 22).\[^{38-39}\]

![Scheme 22: Radical addition to a triple bond.](image)
A.3.2 SF₅-compounds from arylsulfur chlorotetrafluoride

The synthesis of SF₅-containing compounds from thiols and disulfides via an arylsulfur chlorotetrafluoride has been established by Umemoto and coworkers.\[47\] This method is a practical and economical way of obtaining aryl pentafluorides.

In 1997, Janzen et al. reacted diaryl disulfide with XeF₂ and tetraethylammonium chloride and found that cis- and trans- phenyl sulfur chlorotetrafluoride was formed.\[48\] Thus, they were not able to isolate this compound. Umemoto and his coworkers discovered that arylsulfur chlorotetrafluoride is also formed by treatment of a diaryl disulfide with an excess of chlorine in the presence of an excess of alkaline metal fluoride.\[47\] They prepared different SF₄Cl-compounds from diaryl disulfides and aryl thiols (Scheme 23).

<table>
<thead>
<tr>
<th>R¹</th>
<th>Disulfide</th>
<th>Thiol</th>
<th>ZnF₂</th>
<th>aq HF</th>
<th>HF-Pyridine</th>
<th>SbF₅/SbF₅</th>
<th>SbF₅</th>
</tr>
</thead>
</table>

Scheme 23: Preparation of arylsulfur chlorotetrafluorides.
The reaction was carried out in dry acetonitrile with ca. 16 mol spray dried KF or CsF and ca. 7 mol Cl₂ per mol of the starting compound. The expected product was obtained in high yields with a high purity after distillation.

The reaction of 1 mol diaryl disulfide theoretically needs 5 mol Cl₂ and 8 mol KF.

\[
\text{ArSSAr} + 5 \text{Cl}_2 + 8 \text{KF} \rightarrow \text{1 ArSF}_4\text{Cl} + 8 \text{KCl}
\]

Umemoto postulated a reaction mechanism, showing that the reaction undergoes five intermediates (Scheme 24).\[47\] In the beginning of the reaction, when the chlorine gas is introduced in the reaction mixture, the color changes to orange. A fast absorption of chlorine takes place until step 4. After the Ar-SF₃ has been formed, the reaction mixture becomes colorless. Step 5 and 6 are comparable slow, probably because of the equilibrium reaction in step 5.

\[
\begin{align*}
1/2\text{ArSSAr} \quad & \xrightarrow{\text{step 1}} \quad 1/2\text{Cl}_2 \quad \xrightarrow{\text{step 2}} \quad \text{Ar-SCI} \quad \xrightarrow{\text{step 3}} \quad \text{Ar-SFCl}_2 \\
\text{Ar-SF}_3 \quad & \xrightarrow{\text{step 4}} \quad \text{Ar-SF}_4\text{Cl} \quad \xrightarrow{\text{step 5}} \quad \text{Ar-SF}_4\text{K}^+ \quad \xrightarrow{\text{step 6}} \quad \text{Ar-SF}_4\text{Cl} \\
\end{align*}
\]

Scheme 24: Mechanism by Umemoto\[47\].

The obtained SF₄Cl-compound is not stable in glass and has to be stored in fluoropolymer bottles.

For the conversion of an arylsulfur chlorotetrafluoride to the corresponding pentafluoride, Umemoto used different fluorination agents.\[47\]

The reaction with ZnF₂ needs high temperatures with 90°C and higher. The reaction time is in the majority of cases more than 15 hours and the desired SF₅-compound was obtained with 36 to 79% yields (Scheme 25).
Compared to the ease to handle ZnF₂, the usage of HF is difficult, due to the high toxicity. The reaction with anhydrous HF runs at low temperatures (−10 to 20°C) and has a reaction time of 17 to 48 h giving the desired products in 56-77% yield. For some compounds additives like KHF₂ or PhH were needed to obtain the product. The phenyl-SF₄Cl was also treated with HF-pyridine at 55°C for 3 h to give the desired SF₅-phenyl with 63% yield (Scheme 26).

Another method uses antimony fluorides. The combination of SbF₃ and a strong Lewis acid (SbF₅ or SbCl₅) works for polyfluorinated compounds with good yields. The reaction is done at r.t. or lower in not more than 5 h. For aryl bis- and tris-sulfur pentafluorides the usage of SbF₅ at higher temperatures up to 95°C gives the desired products in good yields (Scheme 27).
Scheme 27: Reaction using antimony fluorides.
A.4 Pentafluorosulfanyl aromatics

SF₅-containing aromatics can be useful building blocks for many different SF₅-compounds. Until now, only a few methods for the synthesis of SF₅-containing aromatics are known.

In 1962, Sheppard found a method to synthesize SF₅-containing aromatics using silver difluoride. The starting reagents, aryl disulfides or arylsulfur trifluorides, are fluorinated with AgF₂ to produce an SF₃-substituted aromatic compound as shown in Scheme 28. A second fluorination leads to the SF₅-containing aromatic. Silver difluoride, though, is an expensive reagent and the yields of this reaction are only 5-14%.

Another method of obtaining SF₅ aromatics was published by Seppelt et al. in 1986. Pentafluorosulfanylacetylene was reacted with Co₂(CO)₈ to give the complex Co₂(CO)₄(HC=CSF₅)₃. In the presence of Br₂, the complex decomposed to 1,2,4-tris(pentafluorosulfanyl)benzene in 88% yield (Scheme 29).
Theoretical Background

Scheme 29: Synthesis of SF$_5$-containing aromatics by J. Wessel, H. Hartl and K. Seppelt.

Another SF$_5$-benzene can be obtained by photoreaction of pentafluorosulfanlylacetylen in the presence of SF$_5$Cl and gives 1,3,5-tris(pentafluorosulfanyl)benzene (Scheme 30)$^{[50]}$

Scheme 30: Synthesis of SF$_5$-containing aromatics using irradiation by K. Seppelt et al.

Pentafluorosulfanlylacetylen is obtainable from acetylene, reacted with SF$_5$Cl. Bromination with Br$_2$ under UV irradiation, dehydrobromination and reduction with zinc gives the pentafluorosulfanlylacetylen.$^{[50]}$

Bowden, Comina, Greenhall, Kariuki, Loveday and Philp developed a method using thiophenols, aromatic methyl thioethers and disulfides as starting compounds.$^{[51]}$ As shown in Scheme 31, the SF$_5$-containing aromatics are synthesized via direct fluorination with F$_2$. The starting compound is dissolved in anhydrous acetonitrile at a temperature of -5°C and a steady stream of a mixture of F$_2$/N$_2$ gas (10% v/v F$_2$) was passed through the reaction mixture. The SF$_5$-products were obtained in low to good yields.

$^{[50]}$ Bowden, Comina, Greenhall, Kariuki, Loveday and Philp developed a method using thiophenols, aromatic methyl thioethers and disulfides as starting compounds.}$^{[51]}$ As shown in Scheme 31, the SF$_5$-containing aromatics are synthesized via direct fluorination with F$_2$. The starting compound is dissolved in anhydrous acetonitrile at a temperature of -5°C and a steady stream of a mixture of F$_2$/N$_2$ gas (10% v/v F$_2$) was passed through the reaction mixture. The SF$_5$-products were obtained in low to good yields.
Sergeeva and Dolbier developed a new synthesis of pentafluorosulfanylbenzene in 2004.\cite{8} The three-step synthesis of pentafluorosulfanylbenzene from 1,4-cyclohexadiene led to the product with an overall yield of more than 70%. In the first step the diene is reacted with $\text{SO}_2\text{Cl}_2$ in $\text{CCl}_4$ at room temperature to get 4,5-dichlorocyclohexane. After the $\text{BEt}_3$ catalyzed radical addition of $\text{SF}_5\text{Cl}$ in $\text{CH}_2\text{Cl}_2$ at $-20^\circ\text{C}$, treatment with $\text{NaOEt}$ in $\text{EtOH}$ at ambient temperature for 15 h renders pentafluorosulfanylbenzene with an overall yield of more than 70% (Scheme 32).

As already mentioned before, Umemoto obtained $\text{SF}_5$-containing aromatics from aryl sulfur compounds.\cite{8} These compounds were reacted with a halogen and a fluoro salt to form aryl sulfur halotetrafluoride. Treatment with a fluorine source leads to the aryl sulfur pentafluoride (Scheme 33).
The utilization of SF$_5$-containing aromatics can lead to a variety of important and useful compounds.

Beier et al. reported a method to obtain (E)-2-nitro-1-alkenyl-(pentafluorosulfanyl)benzenes.$^{[52]}$

Nucleophilic substitution reaction of meta- and para-nitro-(pentafluorosulfanyl)benzenes and diethyl chloromethylphosphonate gives diethyl 2-nitro-(pentafluorosulfanyl)benzylphosphonates. Treatment with aldehydes in the presence of potassium hydroxide in acetonitrile at ambient temperature in a Horner–Wadsworth–Emmons reaction leads to the desired (E)-2-nitro-1-alkenyl-(pentafluorosulfanyl)benzenes. The reaction shows a high stereo selectivity and good yields (Scheme 34).
Further reactions were used to transform the \((E)\)-2-nitro-1-alkenyl-(pentafluorosulfanyl)benzenes into \((E)\)-1-alkenyl-(pentafluorosulfanyl)benzenes and 2-(2-arylethyl)-(pentafluorosulfanyl)anilines.

Another interesting utilization reaction was also done in the laboratory of Beier.\(^{[53]}\) Scheme 35 shows the conversion of \(\text{para-}\) and \(\text{meta-}\)nitro-(pentafluorosulfanyl)benzenes to \(\text{SF}_5\)-aryl ethers and sulfides in a single step reaction. Alkoxides and thiolates were used for this nucleophilic aromatic substitution.

\[
\begin{align*}
\text{NO}_2 & \quad \text{R} & \quad \text{Y} & \quad \text{R} \quad \text{Y} \\
\text{F}_5\text{S} & \quad \text{DMF}, \text{ r.t.} & \quad \text{up to 96% yield}
\end{align*}
\]

Scheme 35: Nucleophilic aromatic substitution by Beier.

Methoxy-(pentafluorosulfanyl)benzenes can be transferred furthermore to (pentafluorosulfanyl)phenols or in the case of the \(\text{para-SF}_5\) compound to 2-bromo-1-methoxy-4-(pentafluorosulfanyl) benzenes by regioselective monobromination (Scheme 36).

\[
\begin{align*}
\text{OMe} \quad \text{H} & \quad \text{OH} \\
\text{F}_5\text{S} & \quad \text{DMF}, 110^\circ\text{C}, 1\text{h} & \quad \text{para-SF}_5: 92\% \\
\text{OMe} & \quad \text{Br}_2 (5\text{eq}) & \quad \text{meta-SF}_5: 98\% \\
\text{SF}_5 & \quad \text{AcOH}, 60^\circ\text{C}, 24\text{h} & \quad 81\%
\end{align*}
\]

Scheme 36: Further reactions of methoxy-(pentafluorosulfanyl)benzenes.

This chapter showed a number of different synthetic strategies to obtain \(\text{SF}_5\)-containing compounds, especially aromatics. But expensive reactants, long reaction times and sometimes even low yields show the need of further
research. Since the SF$_5$-group is such an important substituent with growing future perspectives, it is necessary to establish better synthetic routes and make more SF$_5$-containing compounds available for chemical applications.
B Aim of the Work

Preparation of SF$_5$- and CF$_3$-containing aromatics via radical addition of SF$_5$Cl

Different 7-oxa-norbornene derivatives should be prepared as starting compounds for the preparation of SF$_5$-containing aromatics. The first step of the utilization is the radical addition of SF$_5$Cl to the olefin. This reaction will be catalyzed either by UV-irradiation or BEt$_3$. In the second step, different bases as well as Lewis and Brønsted acids shall be investigated for HCl elimination and aromatization.

![Scheme 37: Preparation of SF$_5$-containing aromatics via radical addition of SF$_5$Cl.](image)

The analogous reaction should be conducted using CF$_3$I to obtain CF$_3$-containing aromatics.

Comparing both reactions, the influence of the SF$_5$-group should be investigated.

Preparation of SF$_5$-containing aromatics via arylsulfur chlorotetrafluorides

Different thiols and disulfides should be reacted with Cl$_2$ gas in the presence of KF to obtain the corresponding chlorotetrafluorides. In a second step, the opportunities for the conversion to the SF$_5$-compound should be investigated.
Aim of the Work

Scheme 38: Preparation of SF$_2$-containing aromatics via arylsulfur chlorotetrafluorides.
C Results and Discussion

C.1 Preparation of SF$_5$- and CF$_3$-containing aromatics via radical addition of SF$_5$Cl and CF$_3$I

The radical addition of SF$_5$Cl to the double bond of a 7-oxa-norbornene cage and the following ring opening and aromatization is a new method to synthesize aromatic SF$_5$-containing compounds. In this dissertation, different derivatives have been examined for their use as building blocks. Additionally, the synthesis of CF$_3$-analogues via radical addition of CF$_3$I has been investigated to compare the reactivity and usefulness of the methods.

C.1.1 Preparation of SF$_5$-containing naphthalene

Different groups have done preparation of naphthalenes from 1,4-dihydro-1,4-epoxynaphtalene derivatives in the past. Smith, et al. used trimethylsilyl chloride and sodium iodide.$^{[54-55]}$ BF$_3$-Et$_2$O was used by Sugahara et al. resulting in 1-pyridynaphthalenes.$^{[56]}$

Schlosser and Castagnetti used two methods for aromatization of 7-oxa-norbornen derivatives with an OCF$_3$-group.$^{[57]}$ Concentrated hydrochloric acid (32% aq) was added to a methanolic solution of 7-oxa-norbornen. Refluxing the mixture for 2 h led to the aromatic product in a yield of 73%. In the second approach, the 7-oxa-norbornen was dissolved in acetic acid and a large excess of zinc was added. Refluxing for 20 h gave the expected product in 71% yield (Scheme 39).
Reactions involving 1,4-dihydro-1,4-epoxynaphtalenes substituted with electron withdrawing groups have been studied by different research groups. Bailly et al. prepared a naphthalene derivative from a bromo-substituted epoxynaphthalene using t-BuOK as a base. This reaction led to a mixture of the aromatization product and a product of HBr elimination in a 1:1 ratio (Scheme 40a). An aromatization reaction with epoxynaphthalene substituted with an electron withdrawing group like CO₂H has been accomplished by Smith et al. P₂S₅/CS₂ and NaI/Me₃SiCl have been used for the aromatization (Scheme 40b).

The derivatization of 7-oxa-norbornenes with an SF₅-group attached directly to the norbornene cage was studied, which has not been investigated before.

The starting compound 1,4-dihydro-1,4-epoxynaphtalene 1 was synthesized from bromophenol 1a reacted with HMDS at 80°C for 45 min. The
bromophenoxy trimethylsilane 1b was treated with BuLi to give the lithium phenolate 1c, which was reacted with triflic anhydride to form the dienophile 1d. Diels-Alder reaction of 1d with furan led to 1,4-epoxynaphthalene 1 (Scheme 41).

![Scheme 41: Preparation of 1,4-dihydro-1,4-epoxynaphtalene 1.]

For the radical addition of SF₅Cl to the 7-oxa-norbornene derivative 1, BEt₃ was used as low temperature initiator. In a glass ampoule, 1,4-dihydro-1,4-epoxynaphtalene 1 was dissolved in dry dichloromethane and cooled down using liquid nitrogen. 2 eq of SF₅Cl were condensed into the reaction mixture and 0.03 eq triethylborane was added. The mixture was stirred at -30 to -25°C for 5 h and over night at ambient temperature. The addition product 2 was obtained after workup and column chromatography in 41% yield.

![Scheme 42: Radical addition of SF₅Cl to 1,4-dihydro-1,4-epoxynaphtalene 1.]

After addition of SF₅Cl, HCl elimination was carried out. Different bases were examined to find the best suitable method. In one attempt 5 eq of K₂CO₃ in DMF was used. This reaction was carried out at ambient temperature and at
60°C. In another attempt 1.1 eq DBU in dry hexane at ambient temperature was applied at 60°C. A third method used 5 eq LiOH in dry DMSO at 60°C. Every reaction was carried out for several days. The formation of products was monitored by 19F-NMR.

Scheme 43: HCl elimination.

Table 3: HCl elimination of 2 with different bases.

<table>
<thead>
<tr>
<th>base</th>
<th>temperature</th>
<th>reaction time</th>
<th>results</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂CO₃</td>
<td>r. t.</td>
<td>20h</td>
<td>no reaction</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>60°C</td>
<td>3d</td>
<td>83% product, side products</td>
</tr>
<tr>
<td>DBU</td>
<td>r. t.</td>
<td>20h</td>
<td>no reaction</td>
</tr>
<tr>
<td>DBU</td>
<td>60°C</td>
<td>2d</td>
<td>decomposition of starting compound</td>
</tr>
<tr>
<td>LiOH</td>
<td>60°C</td>
<td>12h</td>
<td>69% product, no side products</td>
</tr>
</tbody>
</table>

The approach with K₂CO₃ and DBU at ambient temperature showed no reaction. Heating the reaction with DBU led to decomposition of the starting compound. Using K₂CO₃ at 60°C and LiOH at 60°C led to the desired product, yet only in the reaction with LiOH was the product obtained without any side products. Additionally, the reaction was complete after only 12 h compared to the reaction time of 3 d for K₂CO₃.

Aromatization of 5-pentafluorosulfanyl-7-oxabicyclo[2.2.1]hept-5-ene 3 was carried out using two different methods. The starting compound was dissolved in acetic acid and 10 eq activated zinc was added. The reaction mixture was heated under reflux for 15 h. The reaction failed to give the desired product; only the starting compound was detected.
Results and Discussion

In the second approach, the starting compound was dissolved in methanol and hydrochloric acid was added. The reaction mixture was first stirred at 50°C for 3 days and then stirred at 70°C for another 2 days. One main aromatization product was detected.

Theoretically, two aromatization products are possible to yield from this reaction, but only the product with the hydroxy group in o-position to the pentafluorosulfanyl group was detected. This can be explained by the thermodynamic stability of the carbocation. The positive charge is less stabilized in direct vicinity to the electron withdrawing SF₅-group.

The structure of the product with the hydroxy group in o-position to the pentafluorosulfanyl group was proven by X-ray analysis.
In literature, only a few X-ray structures of SF$_5$-containing aromatics are known, Table 4 shows some examples.

Compound 14 crystallizes in the monoclinic space group \emph{P}2$_1$/c. The bond length of the S-C bond is 1.795 Å, which is in the normal range, comparatively. The angles of the equatorial fluorine atoms with the sulfur and carbon atom are larger than 90°, measuring about 93°. The SF$_5$-group shows the typical “umbrella shape” with the equatorial fluorines bent away from the aromatic ring. This is not only known for C-SF$_5$ compounds, as shown in Table 4, but also compounds with the SF$_5$-group connected to nitrogen show this confirmation.\cite{60} The bond lengths of the S-F bonds vary from 1.578 Å to 1.597 Å. The hydroxy group is bent away from the SF$_5$-group, with an O-C-C angle of 125.7° towards the SF$_5$-goup and an O-C-C angle of 112.4° away from the SF$_5$-group.
Table 4: Crystallographic data (values for bond length S-F_{eq}, angle F_{ax}-S-F_{eq} and angle C-S-F_{eq} are average values).

<table>
<thead>
<tr>
<th>structure</th>
<th>space group</th>
<th>bond length C-S (Å)</th>
<th>bond length S-F_{eq} (Å)</th>
<th>bond length S-F_{ax} (Å)</th>
<th>angle F_{ax}-S-F_{eq}</th>
<th>angle C-S-F_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>monoclinic P2_{1}/c</td>
<td>1.795</td>
<td>1.588</td>
<td>1.596</td>
<td>87.05°</td>
<td>93.05°</td>
</tr>
<tr>
<td>a[^61]</td>
<td>orthorhombic Pbac</td>
<td>1.786</td>
<td>1.582</td>
<td>1.600</td>
<td>86.93°</td>
<td>93.18°</td>
</tr>
<tr>
<td>b[^62]</td>
<td>monoclinic C_{2}/c</td>
<td>1.807</td>
<td>1.5717</td>
<td>1.5792</td>
<td>87.91°</td>
<td>92.12°</td>
</tr>
<tr>
<td>c[^18]</td>
<td></td>
<td>1.8066</td>
<td>1.5827</td>
<td>1.5791</td>
<td></td>
<td>92.31</td>
</tr>
<tr>
<td>d[^63]</td>
<td>orthorhombic Cmcm</td>
<td>1.812</td>
<td>1.576</td>
<td>1.581</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e[^63]</td>
<td>monoclinic C_{2}/c</td>
<td>1.795</td>
<td>1.574</td>
<td>1.576</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f[^64]</td>
<td>orthorhombic P2_{1}2_{1}2_{1}</td>
<td>1.81</td>
<td>1.58</td>
<td>1.58</td>
<td>87°</td>
<td></td>
</tr>
<tr>
<td>g[^64]</td>
<td>orthorhombic Pca2_{1}</td>
<td>1.81</td>
<td>1.58</td>
<td>1.58</td>
<td>87°</td>
<td></td>
</tr>
<tr>
<td>h[^65]</td>
<td>monoclinic P2_{1}/n</td>
<td>1.804</td>
<td>1.561</td>
<td>1.587</td>
<td>87.6°</td>
<td></td>
</tr>
</tbody>
</table>

Figure 10: Structures of the X-ray data.
C.1.2 Preparation of CF$_3$-containing naphthalene

F. Benning and coworkers first synthesized CF$_3$-naphthalene in 1942.$^{[66]}$ They heated naphthene, carbon tetrachloride, copper bronze and anhydrous HF in an autoclave up to 155°C for 48 h and obtained trifluoromethyl-naphthalene.

In 1982, Umemoto and Miyano established a new reagent for the photochemical trimethylation of aromatic compounds.$^{[67]}$ Previous reports used trifluoromethyl iodide,$^{[68]}$ but in order to increase the yields and reduce the reaction time, Umemoto and Miyano applied N-trifluoromethyl-N-nitrosobenzenesulfonamide (TNS-B). The aromatic compound, biacetyl as a sensitizer and TNS-B were irradiated under water bath cooling with a 400W high-pressure Hg lamp and gave the desired product with moderate yields. The CF$_3$-naphthalene was obtained in 39% yield (Scheme 46).

![Scheme 46: Synthesis of CF$_3$-naphthalene by Umemoto and Miyani.](image)

Chen and Wu found another methylation agent in 1989.$^{[69]}$ Methylfluorosulfonyldifluoroacetate in the presence of copper(I)iodide forms a complex [CF$_3$CuI], which can be used as trifluoromethylation reagent on alkyl and aryl halides. CF$_3$-naphthalene is obtained from naphthalene bromide or iodide in good yields (Scheme 47).

![Scheme 47: Trifluoromethylation by Chen and Wu.](image)
Other synthetic strategies emanate from naphthalene chloride using [(allyl)PdCl]_2 or Pd(dba)_2, or from arylboronates via oxidative trifluoromethylation using (trifluoromethyl)trimethoxyborate in the presence of copper acetate as mediator and molecular oxygen as oxidant in DMSO.

In 2004, Bailly et al. reported the synthesis of CF₃-naphthalene from 1,4-epoxy-1,4-dihydro-5-(trifluoromethyl)naphthalene. This compound was obtained from 2-chlorobenzotrifluoride, which was treated with butyl lithium and then reacted with furan.

Reaction of 1,4-epoxy-1,4-dihydro-5-(trifluoromethyl)naphthalene with TiCl₄ and Zn powder in THF gave the expected CF₃-naphthalene with 83% yield. Treatment of the starting compound with ethanolic HCl lead to the acid-catalyzed ring opening and gave 8-trifluoromethyl-1-naphthol as the only product in 81% yield (Scheme 48).

![Scheme 48: Synthesis of CF₃-naphthalene by Bailly et al.](image)

There are no reported investigations into the acid-catalyzed ring opening of an epoxynaphthalene with the CF₃-group directly connected to the norbornene cage. Therefore this was chosen to be part of the focus in this work.

For the introduction of the CF₃-group, radical addition of CF₃I was used. Dmowski et al. have established a useful method. The starting compound was dissolved in a mixture of water and acetonitrile (1:1) in a closed ampoule and 1 eq sodium dithionite (Na₂S₂O₄) and 2 eq sodium phosphate (Na₃PO₄) were added. The reaction mixture was cooled down using liquid nitrogen and
1.5 eq of the CF$_3$I was condensed into it. After warming up to room temperature, the mixture was stirred for 6 days, then filtered and the solvent was removed under vacuum. The product was dissolved in dichloromethane and washed with water. Purification by column chromatography led to the pure addition product in 92% yield.

\[
\text{CF}_3\text{I} (1.5\text{eq}) \quad \text{CH}_3\text{CN}/\text{H}_2\text{O}, \text{Na}_3\text{PO}_4/\text{Na}_2\text{S}_2\text{O}_4 \quad \text{r.t., 6d}
\]

Scheme 49: Radical Addition of CF$_3$I to 1,4-dihydro-1,4-epoxynapthalene.

For the elimination of HI from the addition product the compound 6 was treated with 5 eq LiOH in DMSO at 50°C for 12 h. The elimination product was obtained in 64% yield.

\[
\text{LiOH} (5\text{eq}) \quad \text{DMSO, 50°C 12h}
\]

Scheme 50: Dehydrohalogenation of 6.

In order to transfer the compound 7 into the desired naphthalene an acid-catalyzed ring opening was operated. Compound 7 was dissolved in a mixture of methanol and 38%-hydrochloric acid (3:1) and was stirred at 75°C for 12 h. After workup two products were detected. The main product 2-trifluoromethyl-1-napthol 8 was isolated in 41% yield. Additionally, a product derived from the hydrolysis of the CF$_3$-group 9 was detected.
Although the CF$_3$-group is known to be stable against basic hydrolysis at low temperatures,$^{[2]}$ it has been reported, that hydrolysis of the trifluoromethyl group can occur either when heated to high temperatures$^{[74]}$ or when treated with acids like aqueous hydrochloride acid.$^{[75]}$ Under the conditions used in this work, the hydrolysis took place, but only in a small amount. The main product is the desired aromatization product 8.
C.1.3 Preparation of SF$_5$-containing dimethyl phthalate

Dimethyl 7-oxanorbornene-2,3-dicarboxylates are found to be suitable starting compounds for aromatization reactions. Different examples from literature show their usefulness to prepare aromatics.

Sarkar et al. showed an aromatization reaction of a dimethyl 7-oxanorbornene-2,3-dicarboxylate with DBU in benzene and obtained the aromatic product in 45-55% yield (Scheme 52a). Smith and co-workers reported the derivatization of a similar starting compound with $p$-toluenesulfonic acid monohydrate in toluene in 65% yield (Scheme 52b). 

![Scheme 52: Aromatization of dimethyl 7-oxanorbornene-2,3-dicarboxylates.](image)

Also strong bases like KHMDS and LHMDS were used for ring opening of the THF ring of dimethyl 7-oxanorbornene-2,3-dicarboxylates, but the disadvantage of those reagents is that they could destroy sensitive side groups.

In this work, an SF$_5$-containing dimethyl 7-oxanorbornene-2,3-dicarboxylate will be used for aromatization reaction.

The radical addition of SF$_5$Cl has been investigated to the dimethyl 7-oxanorbornene-2,3-dicarboxylate 11, but also to 7-oxabicyclo[2.2.1]hept-5-
ene-2,3-dicarboxylic anhydride 10. The preparation of the starting compound was performed via Diels-Alder reaction from maleic anhydride and furan to obtain 10 and following esterification reaction for the conversion to 11.

\[
\begin{align*}
\text{ether, r.t.} & \quad \text{ether, r.t.} \\
\text{H}_2\text{SO}_4, \text{MeOH} & \quad \text{H}_2\text{SO}_4, \text{MeOH}
\end{align*}
\]

Scheme 53: Preparation of 11.

The addition of SF\textsubscript{5}Cl to 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride 10 was investigated using two different initiators. It has been well established that radical addition of SF\textsubscript{5}Cl to a double bond is much easier to achieve when added to a terminal double bond.\[^8\] Addition to a cyclic double bond is more difficult; therefore we employed a large excess of SF\textsubscript{5}Cl with a longer reaction time in the following reactions.

In the first attempt, UV-irradiation was used for initiation. 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride 10 was dissolved in dichloromethane and cooled down using liquid nitrogen. SF\textsubscript{5}Cl was condensed into the reaction mixture, which was warmed up to ambient temperature and irradiated with UV light overnight. However, this attempt failed, resulting in only trace amounts of the desired product (Scheme 54a).

The second reaction utilized BE\textsubscript{3} as low temperature initiator. The reaction was carried out in an open system using a dry ice condenser. 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride 10 was dissolved in dry dichloromethane and cooled down using liquid nitrogen. 3.5 eq of SF\textsubscript{5}Cl was condensed into the reaction flask and 0.03 eq triethylborane was added as low temperature initiator. The mixture was stirred at -30 to -25 °C for 12 h then warmed up to ambient temperature and stirred over night. After workup and column chromatography the addition product 12 was obtained in 56% yield (Scheme 54b).
Results and Discussion

Scheme 54: Radical Addition of SF₅Cl to 10.

After addition of SF₅Cl, the anhydride was transferred into the dimethyl-7-oxanorbornene-2,3-dicarboxylate by treatment with catalytic amounts of H₂SO₄ in methanol, resulting in product 13 in 90% yield.

Scheme 55: Dicarboxylation of 11.

For the radical addition of SF₅Cl to the dicarboxylate 11 we used triethylborane for the initiation. Similar to the reaction with the anhydride 10, 11 was dissolved in dry dichloromethane and cooled down with liquid nitrogen. 3.5 eq SF₅Cl was condensed into the reaction mixture and it was stirred at -40°C for 8 h. After warming up to ambient temperature it was stirred for another 12 hours. After workup, chromatography was operated and the product was obtained in 79% yield.
Results and Discussion

For the elimination of HCl and aromatization, different approaches have been attempted (Table 3). The reaction progress and formation of products were monitored by $^{19}$F-NMR.

Scheme 56: Radical Addition of SF$_5$Cl to 11.

Scheme 57: HCl elimination and aromatization of 13.

Table 5: Results of HCl elimination and aromatization of 13.

<table>
<thead>
<tr>
<th>Base</th>
<th>Solvent</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHMDS</td>
<td>THF</td>
<td>decomposition of the SF$_5$ group in starting compound, formation of 15 in 10-15% yield</td>
</tr>
<tr>
<td>t-BuOK</td>
<td>THF</td>
<td>decomposition of the SF$_5$ group in starting compound</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>Acetone</td>
<td>Mixture of many compounds</td>
</tr>
<tr>
<td>Et$_3$N</td>
<td>-</td>
<td>no reaction</td>
</tr>
<tr>
<td>KOH</td>
<td>Ether</td>
<td>Mixture of many compounds</td>
</tr>
<tr>
<td>K$_2$CO$_3$</td>
<td>DMF</td>
<td>formation of 15</td>
</tr>
<tr>
<td>DBU</td>
<td>CH$_2$Cl$_2$</td>
<td>formation of 15</td>
</tr>
<tr>
<td>LiOH</td>
<td>DMSO-</td>
<td>formation of 15</td>
</tr>
</tbody>
</table>
In the first two attempts the strong bases KHMDS and t-BuOK, which are common for aromatization of SF$_5$-free compounds, were employed. In the case of our SF$_5$-substituted compound, the bases were too strong resulting in the decomposition of the SF$_5$ group. Treatment with K$_2$CO$_3$ in acetone and KOH only led to a mixture of many different products without giving the expected aromatization product 14. The reaction with DBU gave a black mixture of polymers, the attempt using NEt$_3$ showed no reaction; only the starting compound was detected.

The last three attempts showed the formation of a product of SF$_5$-elimination as a main product. For the one with DBU, compound 13 was dissolved in dichloromethane and 1.2 eq DBU was slowly dropped into the stirred solution. The reaction mixture became brown right after addition and was stirred at ambient temperature for 12 hours. After workup, no SF$_5$-containing aromatic was detected. But the nortricyclic compound 15 was formed with a 41% yield (Scheme 58a).

For the other approach, compound 13 was dissolved in DMSO and 5 eq LiOH was added. The reaction time at ambient temperature was 24 h. Again, no product of aromatization was detected, but 15 was obtained with 53% yield (Scheme 58b). Also the reaction with K$_2$CO$_3$ in DMF led to the formation of 15 in 45% yield. The mixture of starting compound 13 in DMF and 2 eq K$_2$CO$_3$ was stirred at ambient temperature for 12 hours (Scheme 58c).
Instead of the expected aromatization accompanied with the dehydrohalogenation, the elimination of the SF$_5$-group and the formation of a new ring were observed. It is proposed that all three reactants, DBU, LiOH and K$_2$CO$_3$ induce the formation of the anion 13a. For the stabilization of the compound, elimination and ring closure take place (Scheme 59).

It is known in literature that the SF$_5$-group can act as a leaving group under certain conditions. Dolbier and Zheng reported an unexpected elimination during the synthesis of SF$_5$-containing pyrrols.$^{[46]}$ They attempted a van Leusen synthesis of SF$_5$-pyrroles, but instead of the expected elimination of tosylate, an SF$_5$-free product was obtained.
Scheme 60: SF₅-elimination.

Results and Discussion
C.1.4 Preparation of CF$_3$-containing dimethyl phthalate

Up to now, dimethyl 4-(trifluoromethyl)phthalate has only been prepared via Diels–Alder-reaction. Schlosser et al. reported about the reaction emanating from dimethyl acetylenedicarboxylate and (E)-1-ethoxy-3-trifluoromethyl-1,3-butadiene being heated at 100°C for 16h.$^{[80-81]}$

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{O} \\
\text{OEt} & + \\
\text{100°C, 16h} & \quad \text{CO}_2\text{Me} \\
\text{100°C, 16h} & \quad \text{CO}_2\text{Me} \\
\text{F}_3\text{C} & \quad \text{CO}_2\text{Me} \\
& \quad 78\% \\
\end{align*}
\]

Scheme 61: Synthesis of dimethyl 4-(trifluoromethyl)phthalate.

In this work, the radical addition of CF$_3$I to dimethyl 7-oxanorbornene-2,3-dicarboxylate 11 to obtain the analogous aromatization product was investigated.

The starting compound 11 was dissolved in a mixture of water and acetonitrile (1:1) in an ampoule and 1 eq sodium dithionite and 2 eq sodium phosphate were added. The reaction mixture was cooled down using liquid nitrogen and 1.5 eq of CF$_3$I was condensed into it. After warming up to room temperature, the mixture was stirred for 40 h. Workup and following column chromatography for purification lead to the addition product 16 in 65% yield (Scheme 62).

\[
\begin{align*}
\text{11} & \quad \text{CO}_2\text{Me} \\
\text{CF}_3\text{I (1,5 eq), Na}_3\text{PO}_4/\text{Na}_2\text{S}_2\text{O}_4} & \quad \text{MeCN/H}_2\text{O, 40h} \quad \text{100°C} \\
& \quad \text{CO}_2\text{Me} \\
& \quad \text{CO}_2\text{Me} \\
& \quad \text{65\%} \\
\text{16} & \quad \text{CO}_2\text{Me} \\
& \quad \text{CO}_2\text{Me} \\
& \quad \text{I} \\
& \quad \text{11} \\
\end{align*}
\]

Scheme 62: Radical Addition of CF$_3$I to 11.

For the dehydrohalogenation, different approaches, shown in Table 6, were investigated.
Scheme 63: Dehydrohalogenation and aromatization of 16.

Table 6: Dehydrohalogenation and aromatization of 16.

<table>
<thead>
<tr>
<th>Base</th>
<th>Solvent</th>
<th>Temperature</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH</td>
<td>DMSO</td>
<td>60°C</td>
<td>product with 38% yield</td>
</tr>
<tr>
<td>K₂CO₃</td>
<td>DMSO</td>
<td>60°C</td>
<td>product with 78% yield</td>
</tr>
<tr>
<td>DBU</td>
<td>dichloromethane</td>
<td>r.t.</td>
<td>rearrangement of starting compound</td>
</tr>
<tr>
<td>DBU</td>
<td>dichloromethane</td>
<td>60°C</td>
<td>decomposition of the starting compound</td>
</tr>
</tbody>
</table>

For the first approach, the starting compound 16 was dissolved in DMSO and 2.5 eq LiOH was added. The reaction mixture was heated up to 60°C and stirred for 12 hours. After workup and column chromatography the desired product 17 was obtained in 38% yield (Scheme 64a).

The reaction with potassium carbonate was operated likewise. The starting compound 16 was dissolved in DMSO and 2 eq K₂CO₃ was added. The reaction mixture was stirred for 12 h at 60°C and workup and purification gave the product 17 in 78% yield (Scheme 64b).
The usage of DBU showed a different result. The starting compound 16 was dissolved in dichloromethane and 1.2 eq DBU was dropped into the solution. The reaction mixture was stirred at ambient temperature for 12 h to give a product of rearrangement 18 in 72% yield.

It is proposed that the formation of an anion 16a (Scheme 66), analogous to the reaction with the SF₅-compound 13 (Scheme 59), occurred. Unlike the SF₅-group, the CF₃-group cannot act as a leaving group under these conditions. Instead of the elimination reaction the anion is stabilized via rearrangement of the carboxylic group. The trans-form of the two carboxylic groups is thermodynamically more stable than the cis-form.

Investigating the reaction mixtures of the reactions with lithium hydroxide and potassium carbonate, the intermediate 18 was also detected. It is concluded that the starting compound 16 is converted to the anion 16a and forms intermediate 18. Instead of two endo-hydrogens, 18 contained one endo- and one exo-hydrogen. That brings one to the assumption, that the aromatization

Scheme 64: Reaction with LiOH and K₂CO₃.

Scheme 65: Rearrangement of 16.
process starts with the abstraction of the \textit{exo-\alpha}\)-hydrogen of 18 followed by the C-O bond cleavage of the 7-oxanorbornane cage. The HI elimination and the dehydration finally lead to the formation of the aromatic product 17.

![Reaction mechanism of the formation of 17.](image)

Treatment of the isolated 18 with potassium carbonate under the same conditions as used before also leads to the aromatic product 17 in 69\% yield. Treatment of the starting compound 16 with DBU under heating to 60°C does not lead to aromatization, but causes the decomposition of the corresponding starting compound. The same result is achieved with the reaction of 18 with DBU under heating to 60°C.

The confirmation of the compound 18 was proven by X-ray analysis and is shown in Figure 11.
The crystal structure of 18 proves the configuration with the carboxylic groups in trans position. Table 7 shows examples of crystallographic data from CF₃-aromatics and compares them with our structure. In compound 18, the bond length of the aromatic carbon to the CF₃-carbon is 1.501 Å, which is within the normal range of such a bond, compared to other CF₃-aromatics. The C-F bonds are between 1.335 Å and 1.341 Å, which is only a bit longer than the bond length of the other examples. The angles vary between 111.1° and 113.0° for the C-C-F angle and 111.1° and 113.0° for the F-C-F angles, consistent with the literature.

Table 7: Crystallographic data.

<table>
<thead>
<tr>
<th>structure</th>
<th>bond length C-C(F₃)</th>
<th>bond length C-F</th>
<th>angle C-C-F</th>
<th>angle F-C-F</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.501 Å</td>
<td>1.341 Å</td>
<td>106.7°</td>
<td>111.1°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.335 Å</td>
<td>106.9°</td>
<td>111.7°</td>
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<td></td>
<td></td>
<td>1.337 Å</td>
<td>107.2°</td>
<td>113.0°</td>
</tr>
<tr>
<td>a[82]</td>
<td>1.490 Å</td>
<td>1.310 Å</td>
<td></td>
<td>109.3°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.315 Å</td>
<td></td>
<td>111.9°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.332 Å</td>
<td></td>
<td>116.0°</td>
</tr>
<tr>
<td>b[82]</td>
<td>1.514 Å</td>
<td>1.302 Å</td>
<td>105.1°</td>
<td>111.2°</td>
</tr>
</tbody>
</table>
Results and Discussion

<table>
<thead>
<tr>
<th></th>
<th>1.311 Å</th>
<th>1.325 Å</th>
<th>106.3°</th>
<th>107.6°</th>
<th>112.1°</th>
<th>114.0°</th>
</tr>
</thead>
</table>

Figure 12: Structures of a and b.
C.1.5 Preparation of 1,2-bis(methoxymethyl)-4-(pentafluoro-λ⁶-sulfanyl)benzene

A 1,2-bis(methoxymethyl)-4-(pentafluoro-λ⁶-sulfanyl)benzene has not been known until now. The opportunity to synthesize this new compound via radical addition of SF₅Cl to 5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene and following aromatization was studied.

The starting compound 20 was synthesized from anhydride 10 by ring opening reaction with LiAlH in THF. The mixture was stirred at ambient temperature for 24 hours. For the methylation, 19 was dissolved in dry DMF and was slowly dropped to a mixture of 2.2 eq NaH in DMF. After 30 min 2.2 eq of MeI were added and the reaction mixture was stirred for 30 min at ambient temperature, giving the 5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene 20.

Radical addition of SF₅Cl was operated in an ampoule. Compound 20 was dissolved in dry dichloromethane, cooled down using liquid nitrogen and 2 eq SF₅Cl was condensed into the ampoule. The reaction mixture was warmed up to -30°C and 0.03 eq BEt₃ was added as low temperature initiator. After stirring at -30 to -20 °C for 7 h, the addition product 21 was obtained, after workup and column chromatography, in 96% yield.
For the dehydrohalogenation, compound 21 was dissolved in DMSO and 5 eq LiOH were added. The reaction mixture was heated up to 50°C and was stirred for 24 h. Workup and column chromatography gave the product 22 in 81% yield.

The attempt to react compound 22 with concentrated HCl at 50-75°C for the aromatization, similar to the reactions before, failed.

Treatment of 22 with a mixture of five parts acetic acid and one part sulfuric acid at 100°C for 24 hours led to the formation of the aromatic product 23 in 29% yield. In addition to the acid-induced ring opening and following aromatization, the elimination of one methoxymethyl-group and the hydrolysis of the other took place.

Another approach was the employment of concentrated HCl at higher temperatures than before. Here the starting compound 22 was dissolved in HCl (35% aq) and heated to 100°C. After 90h, 22 was completely consumed.
to give two main products in a complicated mixture. One was a product of chlorination of the methoxymethyl-groups without aromatization, 25, which was isolated in 11% yield. The main product, 24 is a product after acid-induced ring opening of the 7-oxa-norbornene bridge with following aromatization, but also of ring closure of the functional groups forming a THF-ring. It was isolated from the complicated reaction mixture in 56% yield.

![Scheme 71: Aromatization of 22 with HCl.](image)

The structure of product 24 was proven with X-Ray analysis (Figure 13).

![Figure 13: Molecular structure of 24.](image)

The crystallographic date of compound 24 has been compared to the literature data of SF₅-containing aromatics listed in Table 8. It crystallizes in the monoclinic space group \( P2_1/c \). The bond length of the S-C bond is 1.799
Å, similar to known bond lengths of this type. The C-S-F angles for the equatorial fluorines are larger than 90°, as it is known for the SF₅-group, showing the “umbrella shape” with the equatorial fluorines bent away from the aromatic ring. The angle between the axial fluorine and the sulfur and carbon atoms is 179.8°. The bond lengths of the C-F bonds differ between 1.587 Å for the axial and 1.592 Å for the equatorial fluorines.

Table 8: Crystallographic data (values for bond length S-Fₑq, angle Fₑₓ-S-Fₑq and angle C-S-Fₑq are average values).

<table>
<thead>
<tr>
<th>structure</th>
<th>space group</th>
<th>bond length C-S (Å)</th>
<th>bond length S-Fₑq (Å)</th>
<th>bond length S-Fₑₓ (Å)</th>
<th>angle Fₑₓ-S-Fₑq</th>
<th>angle C-S-Fₑq</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
<td>monoclinic P2₁/c</td>
<td>1.799</td>
<td>1.592</td>
<td>1.587</td>
<td>87.43°</td>
<td>92.52°</td>
</tr>
<tr>
<td>a</td>
<td>orthorhombic Pbac</td>
<td>1.786</td>
<td>1.582</td>
<td>1.600</td>
<td>86.93°</td>
<td>93.18°</td>
</tr>
<tr>
<td>b</td>
<td>monoclinic C₂/c</td>
<td>1.807</td>
<td>1.5717</td>
<td>1.5792</td>
<td>87.91°</td>
<td>92.12°</td>
</tr>
<tr>
<td>c</td>
<td>monoclinic C₂/c</td>
<td>1.8066</td>
<td>1.5827</td>
<td>1.5791</td>
<td></td>
<td>92.31°</td>
</tr>
<tr>
<td>d</td>
<td>orthorhombic Cmcm</td>
<td>1.812</td>
<td>1.576</td>
<td>1.581</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>monoclinic C₂/c</td>
<td>1.795</td>
<td>1.574</td>
<td>1.576</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>orthorhombic P₂₁₂₁</td>
<td>1.81</td>
<td>1.58</td>
<td>1.58</td>
<td>87°</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>orthorhombic Pca₂₁</td>
<td>1.81</td>
<td>1.58</td>
<td>1.58</td>
<td>87°</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>monoclinic P₂₁/n</td>
<td>1.804</td>
<td>1.561</td>
<td>1.587</td>
<td>87.6°</td>
<td></td>
</tr>
</tbody>
</table>
Figure 14: Structures of compounds a-h.

Figure 16 shows the $^{19}$F-NMR spectra of product 24. The pentafluoro-$\lambda^6$-sulfanyl-group always shows a characteristic group of signals, due to its AB$^4$-system,$^{83}$ a pentet integrating to one fluorine and a doublet integrating to four fluorines. The fluorines of an SF$_5$-group are in different magnetic environments, one is in axial position and four are in equatorial position.

The A-part shows the axial fluorine coupling with the equatorial fluorines; the doublet (B$^4$-part) represents the four equatorial fluorines coupling with the axial one.

In the spectra of compound 24, the A-part is located at 84.01-85.60 ppm, the doublet of the B$^4$-part at 63.74 ppm. This is within the normal range known from different SF$_5$-containing aromatics.$^{8,22,84}$ The shift is dependent on the structure of the compound, but also on the measurement itself. The coupling constant of the doublet of the B$^4$-part for SF$_5$-aromatics is described to be in a range of 145 to 155 Hz, compound 24 shows a coupling constant of 150 Hz.
An abridgement of the $^{13}$C-NMR spectrum of product 24 is shown in Figure 17. On the left side at 153.5 ppm a double of quintets represents the carbon atom directly attached to the SF$_5$-group. The carbon atom couples to the 4 equatorial fluorines, which leads to the splitting into a quintet with a coupling constant of 17.3 Hz. Also the coupling with the axial fluorine is visible with the splitting of the quintet into a doublet of quintets with the coupling constant of 1.2 Hz. The other two signals represent the carbon atoms in direct vicinity to the SF$_5$-carbon. Here only the coupling with the equatorial fluorines is visible with a coupling constant of 4.7 Hz, the coupling with the axial fluorine is too small.
These characteristic signals are consistent with the spectra of similar compounds from the literature. Phenylsulfur pentafluoride e.g. is described to have coupling constants of 17.2 Hz and 4.7 Hz, respectively.\cite{footnote8}
C.1.6 Preparation of 1,2-bis(methoxymethyl)-4(trifluoromethyl) benzene

1,2-bis(methoxymethyl)-4(trifluoromethyl) benzene is also not known in literature, likewise to its SF5-analogue (C.1.5). In this work, the radical addition of CF3I to 5,6-bis(methoxymethyl)-7-oxa-bicyclo[2.2.1]hept-2-ene 20 and following dehydrohalogenation and aromatization was investigated.

For the radical addition of CF3I to 5,6-bis(methoxymethyl)-7-oxa-bicyclo[2.2.1]hept-2-ene 20, the starting compound was dissolved in a mixture of acetonitrile and water (1:1) in an ampoule, 2 eq. sodium phosphate and 1 eq. sodium dithiolate were added and the mixture was cooled down using liquid nitrogen. 1.5 eq. trifluoroiodomethane were condensed into the ampoule, it was warmed up to ambient temperature and stirred for 2 days. After workup and column chromatography the addition product 28 was obtained in 63% yield.

![Scheme 72: Radical Addition of CF3I to 20.](image)

Treatment of compound 28 with 5eq LiOH in DMSO at 50°C for 12 h led to the product of dehydrohalogenation 29 in 75% yield.

![Scheme 73: Dehydrohalogenation of 29.](image)

The acid-induced ring opening and aromatization with HCl did not give the expected results. The reactions were carried out with 35% HCl in methanol or
without any solvent. The temperatures were tested from 75-100°C for several days, but the product of aromatization 30 was not detected.

Scheme 74: Aromatization of 28.
C.2 Preparation of SF$_5$-containing aromatics via arylsulfur chlorotetrafluorides

Chapter A.3.2 describes the synthetic method established by Umemoto and co-workers to obtain arylsulfur pentafluorides from arylsulfur chlorotetrafluorides.$^{[47]}$ They applied the reagents zinc fluoride, anhydrous hydrogen fluoride, HF-pyridine and antimony fluorides. Although this method cleared the way towards several arylsulfur pentafluorides, optimization in cases of effectiveness, safety and costs is still necessary. In this work, new conditions for the synthesis of SF$_5$-containing aromatics via arylsulfur chlorotetrafluorides were investigated.

C.2.1 Preparation of phenylsulfur pentafluoride

Phenylsulfur pentafluoride is a basic building block for all applications concerning SF$_5$-containing aromatics. Umemoto reported the synthesis of phenylsulfur pentafluoride from phenylsulfur chlorotetrafluoride with two different reagents.$^{[47]}$

The usage of zinc fluoride proceeds with no solvent and high temperatures and leads to the desired product in 75% yield. Treatment of the phenylsulfur chlorotetrafluoride with anhydrous hydrogen fluoride at 15°C for 20 h gave the product in 62% yield.
The starting compound 32 was obtained using an optimized version of the synthesis applied by Umemoto. Diphenyl disulfide 31 was dissolved in dry acetonitrile and 16 eq KF were added. The KF was purchased spray dried, but was further dried under vacuum to obtain ideal conditions. The reaction mixture was cooled down to 0°C and a steady stream of chlorine gas was passed through, giving a yellow/orange color right after the start of streaming. After 8 hours, the reaction mixture was allowed to reach ambient temperature and a color change to white was visible. The chlorine supply was stopped and the reaction mixture was stirred at ambient temperature for 12 hours to give phenylsulfur chlorotetrafluoride, after distillation, in 89% yield.

The observed color changes substantiate the mechanism postulated by Umemoto, showing that the reaction undergoes five intermediates (Scheme 77). On introducing chlorine to the reaction, the mixture turns yellow/orange immediately. A fast absorption of chlorine takes place until step 4. After the PhSF$_3$ has been formed, the reaction mixture becomes colorless. Presumably, because of the equilibrium reaction in step 5, both step 5 and...
step 6 are comparably slow, eventually leading to the expected chlorotetrafluoride.

\[
\begin{align*}
1/2 \text{PhSSPh} & \xrightarrow{\text{step 1}} 1/2 \text{Cl}_2 & \xrightarrow{\text{step 2}} \text{PhSCI} & \xrightarrow{\text{step 3}} \text{PhSF} & \xrightarrow{\text{step 6}} \text{PhSFCl}_2 \\
& \xrightarrow{\text{step 4}} \text{PhSF}_3 & \xleftarrow{\text{step 5}} \text{PhSF}_4^+ \xrightarrow{\text{step 6}} \text{PhSF}_4\text{Cl} \\
& \xrightarrow{2 \text{KF}, -2 \text{KCl}} & \text{PhSF}_3 & \xrightarrow{\text{KF}} & \text{PhSF}_4^+ \xrightarrow{\text{Cl}_2, - \text{KCl}} & \text{PhSF}_4\text{Cl}
\end{align*}
\]

Scheme 77: Steps of reaction from diphenyl disulfide to phenylsulfur chlorotetrafluoride 31.

Compound 32 is not stable in glass and has to be stored in a fluoropolymer bottle. For the conversion of 32 to the desired phenylsulfur pentfluoride 33, several attempts were investigated (Table 9).

\[
\begin{align*}
\text{SF}_4\text{Cl} & \xrightarrow{\text{conditions a to l}} \text{SF}_5 \\
\text{32} & \text{33}
\end{align*}
\]

Scheme 78: Conversion of 31 to the desired phenylsulfur pentfluoride 33.

Table 9: Optimization of conversion of 31 to the desired phenylsulfur pentfluoride 33.

<table>
<thead>
<tr>
<th>eq KHF$_2$</th>
<th>additive</th>
<th>solvent</th>
<th>time</th>
<th>results</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>13</td>
<td>11 eq 48% HF</td>
<td>CH$_2$Cl$_2$</td>
<td>16h</td>
</tr>
<tr>
<td>b</td>
<td>5</td>
<td>0.5 eq TFA</td>
<td>CH$_2$Cl$_2$</td>
<td>16h</td>
</tr>
<tr>
<td>c</td>
<td>2</td>
<td>2 eq TFA</td>
<td>AcOH</td>
<td>3.5h</td>
</tr>
<tr>
<td>d</td>
<td>1</td>
<td>-</td>
<td>MeSO$_3$H</td>
<td>1h</td>
</tr>
<tr>
<td>e</td>
<td>1</td>
<td>-</td>
<td>CF$_3$SO$_2$H</td>
<td>1.5h</td>
</tr>
<tr>
<td>f</td>
<td>2</td>
<td>-</td>
<td>H$_2$SO$_4$</td>
<td>0.5h</td>
</tr>
</tbody>
</table>
Results and Discussion

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>PhSO$_2$Ph</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td>2$^a$</td>
<td>TFA 4h</td>
<td>33 in 100% (59%) yield</td>
</tr>
<tr>
<td>h</td>
<td>1</td>
<td>TFA 1.5h</td>
<td>33 in 100% yield</td>
</tr>
<tr>
<td>i</td>
<td>0.6</td>
<td>TFA 1h</td>
<td>33 in 65% yield</td>
</tr>
<tr>
<td>j</td>
<td>0.6</td>
<td>TFA 6h</td>
<td>33 in 100% yield</td>
</tr>
<tr>
<td>k</td>
<td>1</td>
<td>1 eq TFA 16h</td>
<td>33 in (8%) yield</td>
</tr>
<tr>
<td>l</td>
<td>0.6$^a$</td>
<td>TFA 20h</td>
<td>33 in (82%) yield</td>
</tr>
</tbody>
</table>

The yields were determined by GC/MS, isolated yields are shown in brackets. All reactions had to be conducted in a fluoropolymer flask, due to the low stability of the starting compound in glass.

reaction a)
The starting compound 32 was dissolved in dichloromethane in a fluoropolymer flask and 13 eq KHF$_2$ and 11 eq 45% HF were added. The closed system was stirred overnight at ambient temperature, but after workup no product 33 was detected.

reaction b)
This reaction was also conducted in dichloromethane in a fluoropolymer flask. In this case 5 eq KHF$_2$ and 0.5 eq TFA as additive were added. Stirring the reaction mixture at ambient temperature overnight did not lead to the formation of 33.

reaction c)
Likewise to reaction b, the starting compound was reacted with KHF$_2$ (2 eq) and TFA (2 eq), but in this case acetic acid was used as a solvent. After dissolving of the starting compound 32 in acetic acid and addition of KHF$_2$, TFA was added in three portions after 0, 10 and 20 min. The reaction mixture was stirred at ambient temperature for 3.5 h. After workup no starting compound was detected. But instead of the formation of 33, full conversion of 32 to benzenesulfonyl chloride in 91% yield and benzenesulfonyl fluoride in 9% yield was observed. The attempt to use the very cheap acetic acid for this
reaction failed, with only the hydrolysis of the starting compound to sulfonyl halides taking place.

reaction d)
The next approach investigated the usage of methanesulfonic acid as solvent. After dissolving of 32 in methanesulfonic acid, 1 eq KHF$_2$ was added and the reaction mixture was stirred at ambient temperature for 1 h. Unfortunately, no product, but only starting material was detected.

reaction e)
Triflic acid is a very strong acid, which is supposed to react with the starting compound. 32 is dissolved in triflic acid and the reaction mixture immediately turns orange, also gas evolution is visible. 1 eq KHF$_2$ was added and after 15 min the reaction mixture shows a color change from orange to black. Workup gives a complicated mixture with the expected product 33 in only 5% yield. Additionally, different products of hydrolysis were detected; benzenesulfonyl chloride in 15% yield, benzenesulfonyl fluoride in 14% yield and sulfonyl dibenzene in 9% yield. Triflic acid appears to be a too strong acid for this reaction.

reaction f)
Starting compound 32 was dissolved in concentrated sulfuric acid and 2 eq KHF$_2$ was added. After a few minutes of stirring at ambient temperature, the reaction mixture turns yellow/orange, after further 15 min the color seems to disappear. Workup after another 30 minutes of stirring gave a mixture of different products. The desired product 33 was detected in 14% yield. Unfortunately, the hydrolysis products were also detected; benzenesulfonyl chloride in 44% yield, benzenesulfonyl fluoride in 36% yield and sulfonyl dibenzene in 6% yield. Sulfuric acid as a cheap solvent gives the expected product, but is not suitable for the synthesis because of the hydrolysis reaction competing.

reaction g)
Results and Discussion

In this attempt, TFA is used as a solvent. The starting compound 32 was dissolved in TFA and KHF$_2$ was added in two portions, 1 eq directly and 1 eq after 15 min of stirring at room temperature. After 4 h and subsequent workup the expected product 33 was obtained in 100% yield of conversion and 59% yield after isolation and purification by column chromatography. This result leads to the assumption that the amount of TFA is of high importance. The usage of 1mL TFA for 1mmol of starting material gives the best results.

reaction h)
In order to find the best conditions, investigations on the possibilities of reducing the amount of KHF$_2$ were made. The starting compound was dissolved in TFA and 1 eq KHF$_2$ was added. Only after 1.5 h at ambient temperature, full conversion of the starting material to the desired product 33 was detected.

reaction i and j)
Likewise to reaction h, the amount of KHF$_2$ was even more reduced. Only 0.6 eq KHF$_2$ was added to the starting compound in TFA. After 1h, 65% product was already formed, 35% starting material was still in the mixture. After 68h the reaction was completed, giving only the product 33.

reaction k)
Scale up of the reaction was not trivial. Reaction of the starting compound with 1 eq KHF$_2$ and only a small amount of TFA (30mmol of starting compound in 1 eq TFA) showed a strong evolution of gas and was exothermic. After 1h of stirring at ambient temperature the reaction mixture solidified and 1 eq TFA was added. After a few minutes, the mixture turns orange, after 12 hours the color changes to black. Workup and column chromatography gave the product 33 in only 8% yield.

reaction l)
For the last attempt the scale up is conducted also with a larger amount of TFA. The starting compound is dissolved in TFA (19mmol 32 in 19mL TFA)
and 0.6 eq KHF$_2$ is added in two portions, one directly, the other after 10 min. After workup and column chromatography, the pure product 33 was obtained in 82% yield.

The investigations have shown, that TFA, used as a solvent, and KHF$_2$ as a source for HF are adequate conditions for the conversion of phenylsulfur chlorotetrafluoride to phenylsulfur pentafluoride.

It has been known in literature, that hydrofluoric acid can be generated in situ from trifluoroacetic acid and potassium hydrogen difluoride (Scheme 80).$^{[85-86]}$

This phenomenon was previously used for the HF-mediated nucleophilic fluoroalkylation of imines and enamines to form highly electrophilic iminium fluorides.

In the case of the conversion of phenylsulfur chlorotetrafluoride to phenylsulfur pentafluoride, it is shown that the addition of KHF$_2$ in two portions as well as the amount of TFA respective to the starting material has a great influence on the yield.

The exchange reaction of chlorine to fluorine forms hydrochloric acid, which is a more volatile and stronger acid than HF, the pK$_A$ for HCl is -7, whereas the pK$_A$ for HF is 3.17. Therefor it is concluded that the hydrochloric acid can partially escape the reaction mixture or also react with KHF$_2$ to form KCl and HF to drive the reaction to completion.
The usage of other reactants can lead to hydrolysis, which was not detected with optimized conditions used in this work.

Compared to the results of Umemoto,[47] these conditions are not only more effective, with a yield of 82% (comparatively 75% with zinc fluoride, and 62% with anhydrous HF) but apply also cheaper and safer reagents.
C.2.2 Preparation of 4-Fluorophenylsulfur pentafluoride

4-Fluorophenylsulfur pentafluoride has been synthesized by Umemoto in moderate yields (Scheme 81).\[^{47}\] Likewise to the synthesis of phenylsulfur pentafluoride 33, he applied zinc fluoride and anhydrous hydrogen fluoride for the reaction.

\[ \begin{align*}
\text{SF}_2\text{Cl} & \quad \text{ZnF}_2 \\
\text{F} & \quad 120^\circ \text{C}, 16 \text{h} \\
\text{SF}_5 & \quad 62\% \\
\end{align*} \]

\[ \begin{align*}
\text{SF}_2\text{Cl} & \quad \text{anhyd. HF} \\
\text{F} & \quad 15^\circ \text{C}, 21 \text{h} \\
\text{SF}_5 & \quad 67\% \\
\end{align*} \]

Scheme 81: Synthesis of \( \text{p} \)-fluorophenylsulfur pentafluoride by Umemoto.

In this work, the achievement of better results with the new condition found on the phenylsulfur pentafluoride 33 was asserted.

The synthesis of the starting compound 4-fluorophenylsulfur chlorotetrafluoride 35 was conducted using an optimized version of the method by Umemoto.\[^{47}\]

4-Fluorophenyl disulfide was dissolved in dry acetonitrile and treated with 16 eq spray dried and vacuum dried KF and a steady stream of chlorine gas at 0°C. After 8 hours, the reaction mixture was allowed to reach ambient temperature, the chlorine supply was stopped and the reaction mixture was stirred at ambient temperature for 12 hours. Filtration and distillation was conducted to give the phenylsulfur chlorotetrafluoride in 86% yield.
For the conversion of 35 into the pentafluoride 36, the optimized conditions found in the investigations on compound 33 were applied. The starting compound was dissolved in TFA in a fluoropolymer flask. 0.6 eq KHF$_2$ was added in two portions, one after 0 min, the other after 10 min of stirring at ambient temperature. The flask was closed and the reaction mixture was stirred for 18 h. After workup and purification by column chromatography, the product 36 was obtained in 69% yield.

The new conditions are suitable also for a $p$-fluoro substituted compound and show good results with a slightly higher yield under safer and cheaper conditions than achieved previously by Umemoto.
C.2.3 Preparation of 4-chlorophenylsulfur pentafluoride

Umemoto reported the synthesis of 4-chlorophenylsulfur pentafluoride with zinc fluoride and obtained the product in 73% yield.\[^{47}\] He also applied anhydrous hydrogen fluoride, which gave the product with 71% yield (Scheme 84).

![Reaction Scheme 84](image)

Scheme 84: Preparation of 4-chlorophenylsulfur pentafluoride by Umemoto.

The starting compound 38 was synthesized according to Umemoto’s method using chlorine gas and KF.\[^{47}\] The pure phenylsulfur chlorotetrafluoride was obtained in 81% yield.

![Reaction Scheme 85](image)

Scheme 85: Preparation of 38.

For the synthesis of pentafluoride 39, the starting compound was dissolved in TFA in a fluoropolymer flask. 0.6 eq KHF$_2$ were added in two portions. The best results were achieved with addition of one portion after 0 min, the next after 30 min of stirring at ambient temperature. The flask was closed and the
reaction mixture was stirred for 12h. After workup and purification by column chromatography, the product 39 was obtained in 75% yield.

Applying the new conditions to a \( p \)-chloro substituted phenyl chlorotetrafluoride gives the expected results with a slightly higher yield under milder conditions compared to Umemoto’s work.
C.2.4 Preparation of 4-(tert-butyl) phenylsulfur pentafluoride

4-(tert-Butyl) phenylsulfur pentafluoride is a new compound that has not been synthesized yet. Only the precursor 4-(tert-butyl) phenylsulfur chlorotetrafluoride has been prepared by Umemoto.\(^{[47]}\) He applied CsF as fluoride source and emanated the reaction but from the disulfide, from the thiol compound.

\[
\begin{align*}
&\text{SH} \quad \xrightarrow{\text{Cl}_2(\text{excess}), \text{CsF (10 eq)}} \quad \text{SF}_4\text{Cl} \\
&\text{MeCN, 0°C to r.t., 24h} \quad 84\%
\end{align*}
\]

Scheme 87: Preparation of 4-(tert-Butyl) phenylsulfur chlorotetrafluoride by Umemoto.

In this work, the starting compound 41 was synthesized based on the strategy of Umemoto,\(^{[47]}\) but with the usage of KF instead of CsF, for KF is much cheaper than CsF.

4-(tert-Butyl) phenyl thiol was dissolved in dry acetonitrile and 16 eq spray dried and vacuum dried KF was added. The reaction mixture was cooled down to 0°C and a steady stream of chlorine gas was introduced to the reaction mixture, giving the expected yellow/orange color right after the start of streaming. After 8 hours, the reaction mixture was allowed to reach ambient temperature and the color changed to white. The chlorine supply was stopped and the reaction mixture was stirred at ambient temperature for 12 hours. After filtration, the solvent and the rest of chlorine gas was removed under vacuum and the product was crystallized from hexane to give the pure phenylsulfur chlorotetrafluoride in 55% yield.
The conversion of compound 41 to the corresponding 4-(tert-butyl) phenylsulfur pentafluoride 42 has not been investigated yet by other working groups. We suppose to obtain the product under the conditions, established in this work, via treatment with KHF$_2$ in TFA.

The starting compound was dissolved in TFA in a fluoropolymer flask. 0.6 eq KHF$_2$ were added in two portions, one after 0 min, the next after 30 min of stirring at ambient temperature. The flask was closed and the reaction mixture was stirred for 12h. After workup and purification by column chromatography, the product 42 was obtained in 54% yield.

We were able to obtain the new 4-(tert-butyl) phenylsulfur pentafluoride 42 in moderate yields and showed that our method not only improves the availability of compounds, but also leads to novel structures.
C.2.5 Preparation of 2,4-difluorophenylsulfur pentafluoride

The 2,4-difluorophenylsulfur pentafluoride as well as its precursor 2,4-difluorophenylsulfur chlorotetrafluoride has not been known before. In this work, the influence of the two fluorine substituents on the reactivity of this compound concerning the synthesis of the pentafluoride is investigated.

2,4-Difluorophenyl disulfide was dissolved in dry acetonitrile and treated with 16 eq spray dried and vacuum dried KF and a steady stream of chlorine gas at 0°C, giving a yellow/orange color right after the start of streaming. After 8 hours, the reaction mixture was allowed to reach ambient temperature and the color changed to white. The chlorine supply was stopped and the reaction mixture was stirred at ambient temperature for 12 hours. After filtration and distillation, the pure phenylsulfur chlorotetrafluoride 44 was obtained in 63% yield.

![Scheme 90: Preparation of 44.](image)

The conversion of 44 to the 2,4-difluorophenylsulfur pentafluoride 45 was conducted under similar conditions to the other derivatives.

In a fluoropolymer flask, the starting compound was dissolved in TFA and 1 eq KHF₂ was added in two portions, one after 0 min, the next after 30 min of stirring at ambient temperature. The flask was closed and the reaction mixture was stirred for 12h. However, after workup and purification by column chromatography, no product 45 was detected, only products of hydrolysis (benzenesulfonyl chloride and benzenesulfonyl fluoride).
Results and Discussion

Scheme 91: Preparation of 45.

For the implementation of this reaction, different attempts were investigated (Table 10).

Table 10: Preparation of 45.

<table>
<thead>
<tr>
<th>eq. KHF&lt;sub&gt;2&lt;/sub&gt;</th>
<th>additive</th>
<th>temperature</th>
<th>time</th>
<th>results</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1</td>
<td>r.t.</td>
<td>12h</td>
<td>no 45 detected, formation of PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>b</td>
<td>2</td>
<td>r.t.</td>
<td>24h</td>
<td>no 45 detected, formation of PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>c</td>
<td>3</td>
<td>r.t.</td>
<td>36h</td>
<td>no 45 detected, formation of PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>d</td>
<td>1</td>
<td>50°C</td>
<td>12h</td>
<td>45 in 5.5% yield</td>
</tr>
<tr>
<td>e</td>
<td>1+1</td>
<td>50°C</td>
<td>12h</td>
<td>45 with PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>f</td>
<td>1+2</td>
<td>50°C</td>
<td>12h</td>
<td>45 in 14% yield</td>
</tr>
<tr>
<td>g</td>
<td>1+3</td>
<td>50°C</td>
<td>12h</td>
<td>45 with PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>h</td>
<td>1+2</td>
<td>dry TFA</td>
<td>50°C</td>
<td>45 with PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>i</td>
<td>1+2</td>
<td>tert-Butanol</td>
<td>50°C</td>
<td>45 with PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>j</td>
<td>1+2</td>
<td>hexafluoropr oanol</td>
<td>50°C</td>
<td>45 with PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>k</td>
<td>1</td>
<td>HF-pyridine</td>
<td>50°C</td>
<td>45 with PhSO&lt;sub&gt;2&lt;/sub&gt;Cl and PhSO&lt;sub&gt;2&lt;/sub&gt;F</td>
</tr>
<tr>
<td>l</td>
<td>1</td>
<td>in CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>r.t.</td>
<td>7d</td>
</tr>
</tbody>
</table>
reaction a-c)  
The starting compound 44 was dissolved in TFA in a fluoropolymer flask. 1 eq KHF$_2$ was added and the reaction mixture was stirred at ambient temperature for 12 hours. No product was detected (a). 1eq KHF$_2$ was added and the reaction mixture was again stirred for 12 hours. Still no product has formed (b). A third time 1 eq KHF$_2$ was added, but also after 12 h no product was detected (c).

reaction d)  
In a fluoropolymer flask, 44 was dissolved in TFA and 1 eq KHF$_2$ was added. The flask was closed and heated up to 50°C for 12 h. After workup, a mixture of the product and the hydrolysis products benzenesulfonyl chloride and benzenesulfonyl fluoride was obtained. Treatment of the mixture with NAOH in water, gave the expected product 45 in 5.5% yield.

reaction e-g)  
The starting compound 44 was dissolved in TFA in a fluoropolymer flask. 1 eq KHF$_2$ was added and the reaction mixture was stirred at 30°C for 1 h. More KHF$_2$ (1eq for e, 2eq for f and 3 eq for g) was added and the reaction mixture was stirred at 50°C for 12 h. A mixture of the product with its hydrolysis products was detected. The best ratio of product to hydrolysis products was achieved with reaction f (Scheme 92). The product 45 was isolated in 14% yield.

![Scheme 92: Preparation of 45 with 1+2 eq KHF$_2$.](image-url)
Results and Discussion

reaction h)
This attempt investigated the influence of the moisture content of TFA. TFA was distilled over P₂O₅ and the starting compound was dissolved into it. 1 eq KHF₂ was added right away, the other 2 eq after stirring at 30°C for 1 h. After 12 hours at 50°C, the mixture was analyzed, showing that the ratio product to hydrolysis products is worse that with normal TFA.

reaction i)
The starting compound 44 was dissolved in TFA and 5 eq tert-butanol was added. KHF₂ was added in two portions, 1 eq after 0 min, 2 eq after 1 h at 50°C. The reaction mixture was stirred for 12 h at 50°C, but no product was detected.

reaction j)
To the solution of 44 in TFA, 5 eq of hexafluoropropanol was given. KHF₂ was added in two portions, 1 eq after 0 min, 2 eq after 1 h at 50°C. The reaction mixture was stirred for 12 h at 50°C to give a mixture of the product and the hydrolysis products.

reaction k)
According to the method of Umemoto[47] the starting compound 44 was dissolved in 70% HF-pyridine and stirred at ambient temperature for 15 min. Then the reaction mixture was heated up to 50° and stirred for 3 h. A mixture of the product and the hydrolysis products as main content was observed.

reaction l)
The starting compound 44 was dissolved in dichloromethane and the solution was overlaid with TFA. 1 eq KHF₂ was added and the two phases were stirred at ambient temperature. After one week, still no reaction was observed.

In conclusion, the conversion of 2,4-difluorophenylsulfur chlorotetrafluoride 44 to 2,4-difluorophenylsulfur pentafluoride 45 is not trivial. The most efficient reaction required addition of 3 eq KHF₂ in total, added in two portions of 1 and
2 eq at intervals of 30 min and heating to 50°C. The formation of the hydrolysis products benzenesulfonyl chloride and benzenesulfonyl fluoride could not been suppressed, only lowered. The reaction mixture always needed the treatment with NaOH in water to remove the byproducts. Nevertheless, the aromatic product 45 was obtained in 14% yield.
C.2.6 Preparation of 4-(4-propylcyclohexyl) phenylsulfur pentafluoride

The compound 4-(4-propylcyclohexyl) phenylsulfur pentafluoride has not been synthesized from the analogue chlorotetrafluoride yet, but it is known from the report of Kirsch et al.\textsuperscript{[18]} It was synthesized emanating from 4-(pentafluorosulfanyl) aniline to be investigated as a novel liquid crystal material in an overall yield of 6.3%.

\[ \text{Scheme 93: Synthesis of 4-(4-Propylcyclohexyl) phenylsulfur pentafluoride by Kirsch.} \]

The synthetic strategy in this work starts with the precursor 1,2-bis(4-((1R,4S)-4-propylcyclohexyl)phenyl)disulfane 46.

4-(4-Propylcyclohexyl) phenyl disulfide was dissolved in dry acetonitrile and 16 eq spray dried and vacuum dried KF was added. The reaction mixture was cooled down to 0°C using an ice-bath and a steady stream of chlorine gas was introduced to the reaction mixture, giving a yellow/orange color right after the start of streaming. After 8 hours, the reaction mixture was allowed to reach ambient temperature and the color changed to white. The chlorine
supply was stopped and the reaction mixture was stirred at ambient temperature for 12 hours. After filtration, 4-(4-propylcyclohexyl phenylsulfur chlorotetrafluoride 47 was obtained in 84% yield.

The conversion of the chlorotetrafluoride 47 to the pentafluoride 48 was realized in the following. The starting compound was dissolved in TFA in a fluoropolymer flask. 3 eq KHF₂ was added in two portions, 1 eq after 0 min, the other 2 eq after 30 min of stirring at ambient temperature. The flask was closed and the reaction mixture was stirred for 12h. After workup, the product 48 was obtained in 79% yield.

This result shows, that our method of conversion of a chlorotetrafluoride to a pentafluoride is not only suitable for the synthesis of small building blocks, but
also for the utilization of more complicated substances like the liquid crystal structure used in this studies.
C.2.7 Recovery and reuse of trifluoroacetic acid

The synthesis of arylsulfur pentafluorides from arylsulfur chlorotetrafluorides, established in this work, is a mild and cheap reaction. But for the usage in a big industrial scale, the amount of TFA needed for this reaction could be a point of discussion. Therefore, it has been assumed to show the possibility of the recovery of TFA.

For the study of TFA recovery the reaction of 4-(4-Propylcyclohexyl)phenylsulfur chlorotetrafluoride was investigated. The reaction was performed as described in chapter C.2.6. The starting compound 47 was dissolved in TFA in a fluoropolymer flask. 3 eq KHF$_2$ was added in two portions, 1 eq after 0 min, the other 2 eq after 30 min of stirring at ambient temperature. The flask was closed and the reaction mixture stirred for 12h. Instead of the aqueous workup, the reaction mixture was first distilled in a glass apparatus under normal pressure to recover the TFA. The remaining mixture in the flask could be worked up normally to give the product 48 in 71% yield.

The reaction was repeated with the same substance, but with the recovered trifluoroacetic acid.
Table 11 shows the results.

**Table 11: Recovery and reuse of TFA.**

<table>
<thead>
<tr>
<th>TFA</th>
<th>results</th>
</tr>
</thead>
<tbody>
<tr>
<td>a normal TFA</td>
<td>71% yield</td>
</tr>
<tr>
<td>b recovered TFA</td>
<td>63% yield</td>
</tr>
<tr>
<td>c recovered TFA</td>
<td>70% yield</td>
</tr>
</tbody>
</table>

The yields of the reactions with the recovered TFA are still high. It is shown that it is possible to recover and reuse the TFA. That makes these conditions even cheaper and the amount of corrosive waste is further reduced.
D Conclusion

In this work, two main synthetic strategies for the synthesis of novel SF$_5$- and CF$_3$- containing aromatics were studied. The first is the radical addition of SF$_5$Cl and CF$_3$I to double bonds of 7-oxabicyclo[2.2.1]hept-2-ene derivatives, the second approach is an improved method for the synthesis and following fluorination of arylsulfur chlorotetrafluorides to arylsulfur pentafluorides.

The possibilities for the utilization of 7-oxa-bicyclo[2.2.1]hept-5-ene derivatives for novel SF$_5$-aromatics were investigated. It was shown that the reactivity of 7-oxa-bicyclo[2.2.1]hept-5-ene derivatives towards the radical addition of SF$_5$Cl depends on the structure of the starting olefin. In general, the use of BEt$_3$ for initiation of radical addition gives better yields of the corresponding products than UV-irradiation.

The best results of SF$_5$Cl addition to 7-oxa-bicyclo[2.2.1]hept-5-ene derivatives was achieved in the reaction of 5,6-bis-methoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene 20, the corresponding product 2-pentafluorosulfanyl-3-chloro-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1] heptane 21 was obtained with a high yield, and only 2 eq. of SF$_5$Cl were used. In reactions of 1,4-dihydro-1,4-epoxynaphtalene 1 and 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride 10, a larger excess of SF$_5$Cl and a longer reaction time were used, in order to give the products 1,4-dihydro-2-pentafluorosulfanyl-3-chloro-1,4-epoxynaphtalene 2 and 5-chloro-6-pentafluorosulfanyl-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride 12.

We observed extreme differences in the reactivity of 1,4-dihydro-2-pentafluorosulfanyl-3-chloro-1,4-epoxynaphtalene 2, 6-pentafluorosulfanyl-dimethyl-7-oxanorbornene-2,3-dicarboxylate 13 and 2-pentafluorosulfanyl-3-chloro-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1] heptane 21 in treatment with bases. The best results for HCl elimination from 1,4-dihydro-2-pentafluorosulfanyl-3-chloro-1,4-epoxynaphtalene 2 was obtained using LiOH.
in DMSO. The same system gave satisfactory results in reaction of 2-pentafluorosulfanyl-3-chloro-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]heptane 21, the corresponding product 2-pentafluorosulfanyl-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene 22 was obtained in high yield. Unfortunately, treatment of 6- pentafluorosulfanyl-dimethyl-7-oxanorbornene-2,3-dicarboxylate 13 with bases failed to give the expected product. Only the elimination of the SF$_5$-group was detected, giving dimethyl 5-chloro-3-oxatricyclo[2.2.1] heptane-1,7-dicarboxylate 15.

The reaction of 1,4-dihydro-2-pentafluorosulfanyl-3-chloro-1,4-epoxynaphtalene 2 in methanol with HCl led to the opening of the oxygen bridge, resulting in the aromatization product 1-hydroxy-2-pentafluorosulfanyl-naphthalene 5. Treatment of 2-pentafluorosulfanyl-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene 22 with HCl at room temperature gave no results, but heating up to 100°C gave one aromatization product ( 5-(pentafluorosulfanyl)-1,3-dihydroisobenzofuran 24 ) and a product of chlorination ( 2,3-bis(chloromethyl)-5-(pentafluorosulfanyl)-7-oxabicyclo[2.2.1] hept-5-ene 25). The reaction of 2-pentafluorosulfanyl-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene 22 with a mixture of acetic and sulfuric acid led to the formation of 4-(pentafluorosulfanyl)benzyl acetate 23.

The radical addition of CF$_3$I to 7-oxa-bicyclo[2.2.1]hept-5-ene derivatives shows the best results with 1,4-dihydro-1,4-epoxynaphtalene 1, giving 1,4-dihydro-2-trifluoromethyl-3-ido-1,4-epoxynaphtalene 6. Reactions of 5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene 20 and dimethyl 7-oxanorbornene-2,3-dicarboxylate 11 led to the corresponding products dimethyl 5-iodo-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate 16 and 2-ido-5,6-bis(methoxymethyl)-3-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane 28 with lower yields than the addition to 1.

Treatment of the compounds with bases gave good results. The reaction of 1,4-dihydro-2-trifluoromethyl-3-ido-1,4-epoxynaphtalene 6 with LiOH gave the corresponding product 1,4-dihydro-2-trifluoromethyl-1,4-epoxynaphtalene.
7, 2,3-bis(methoxymethyl)-5-(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-5-ene 29 was obtained from 2-iodo-5,6-bis(methoxymethyl)-3-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane 28, both in good yields. 5-iodo-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate 16 showed good result when treated with $K_2CO_3$ giving the aromatization product dimethyl 4-(trifluoromethyl)phthalate 17. Reaction of 16 with DBU led to the formation of (1S,2R,3S,4S,5R,6R)-dimethyl-5-iodo-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate.

Aromatization reaction of 1,4-dihydro-2-trifluoromethyl-1,4-epoxynaphtalene 7 with HCl led to the formation of 1-hydroxy-2-trifluoromethyl-naphthalene 8, likewise to the reaction with the SF$_5$-analogue 5. Treatment of 2,3-bis(methoxymethyl)-5-(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-5-ene 29 with HCl under different condition did not give the corresponding aromatization product.

In the second part of this work, the synthesis of chlorotetrafluoride compounds from aryldisulfides and arylthiols and the following conversion to the pentafluoro-analogue was investigated.

Treatment of the different precursor with Cl$_2$ and KF led to the formation of phenylsulfur chlorotetrafluoride 32, 4-fluorophenylsulfur chlorotetrafluoride 35, 4-chlorophenylsulfur chlorotetrafluoride 38, 4-(tert-butyl)phenylsulfur chlorotetrafluoride 41, 2,4-difluorophenylsulfur chlorotetrafluoride 44 and 4-(4-propylcyclohexyl)phenylsulfur chlorotetrafluoride 47. For the compounds 32 and 35, the yields were enhanced compared to the literature. Compounds 44 and 47 were synthesized in this work for the first time.

For the fluorination of arylsulfur chlorotetrafluorides to the corresponding arylsulfur pentfluorides, a new method was established. The application of hydrofluoric acid, generated in situ from potassium hydrogen fluoride and trifluoroacetic acid, which also serves as a solvent, is a mild but efficient synthetic method.
Treatment of phenylsulfur chlorotetrafluoride 32 with KHF$_2$ in TFA led to the formation of phenylsulfur pentafluoride 33 in good yields. Also the reaction with 4-fluorophenylsulfur chlorotetrafluoride 35 and 4-chlorophenylsulfur chlorotetrafluoride 38 gave the expected products 4-fluorophenylsulfur pentafluoride 36 and 4-chlorophenylsulfur pentafluoride 39. In all three reactions we were able to enhance the yield compared to the literature. Reaction of 4-(tert-butyl)phenylsulfur chlorotetrafluoride 41 led to the formation of the new product 4-(tert-butyl)phenylsulfur pentafluoride 42. Unfortunately, the direct fluorination of the 2,4-difluorophenylsulfur chlorotetrafluoride 44 caused difficulties and had to be heated up to 50°C in order to obtain the 2,4-difluorophenylsulfur pentafluoride 45. Reaction of 4-(4-propylcyclohexyl)phenylsulfur chlorotetrafluoride 47 succeeded also under the mild conditions at ambient temperature to form the 4-(4-Propylcyclohexyl)phenylsulfur pentafluoride 48 in good yields.

We studied the possibility of the recovery and reuse of TFA, since this is the most expensive reagent in this cheap reaction. We were able to demonstrate the easy recycling of this substance.

In conclusion, this work successfully demonstrated two efficient methodologies to synthesize novel SF$_5$- and CF$_3$-containing aromatics. Both will increase the availability of important building blocks for fluorine chemistry.
E Experimental Part

The $^1$H (400 MHz), $^{13}$C (101 MHz) and $^{19}$F (376 MHz) NMR spectra were recorded on a Bruker DPX-200 spectrometer at ambient temperature using 5mm tubes. Chemical shifts ($\delta$) are reported in ppm relative to Me$_4$Si (0 ppm for $^1$H NMR), residual CHCl$_3$ (7.26 ppm for $^1$H NMR), CDCl$_3$ (77.0 ppm for $^{13}$C NMR), and internal CFCl$_3$ (0 ppm for $^{19}$F NMR). High-resolution mass spectra (HRMS) were recorded on an Agilent 7890A gas chromatograph coupled with a Waters GCT Premier orthogonal acceleration time-of-flight detector using electron impact (EI) or chemical (CI) ionizations.

Column chromatography was performed on Kieselgel Merck 60 (230–400 mesh).

E.1 Preparation of SF$_5$- and CF$_3$-containing aromatics via radical addition of SF$_5$Cl and CF$_3$I

1,4-Dihydro-2-pentafluorosulfanyl-3-chloro-1,4-epoxynaphtalene (2):

In a pressure glass ampoule fitted with a Rotaflo® valve and a magnetic stirring bar, the starting olefin 1 (1.78 g, 12.3 mmol) was dissolved in 20 ml anhyd. dichloromethane. The ampoule was cooled down using liquid nitrogen and evacuated. 2 eq of SF$_5$Cl was condensed into the solution using a vacuum line and the ampoule was warmed up to -40 °C. 0.03 eq BEt$_3$ was added slowly, using a syringe and the solution was stirred for 5-12 h at -25 to -30 °C and then warmed up to r. t. The solvent was evaporated and the pure product was isolated by column chromatography. (yield: 41%)
$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 3.86 (m, 1H), 5.01 (m, 1H), 5.46 (d, 1H, J = 4.8 Hz), 5.88 (s, 1H), 7.30-7.35 (m, 2H), 7.37-7.42 (m, 1H), 7.43-7.46 (m, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 141.68, 141.16, 128.66, 128.27, 123.45, 119.73, 93.69 (quint, J = 10.54 Hz), 83.37 (quint, J = 4.79 Hz), 82.32, 55.49 (quint, J = 3.83 Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 83.8 (9 lines, A-part), 62.6 (dt, J = 146.64, 6.50 Hz, B$_4$-part).

1,4-Dihydro-2-pentafluorosulfanyl-1,4-epoxynaphtalene (3):

![3]

The olefin 2 (0.11 g, 0.34 mmol) was dissolved in 2mL DMSO and 41mg (5 eq) of LiOH was added. The mixture was stirred for 12 h at 60 °C. Water was added and the mixture was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated to obtain the pure product. (yield: 69%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 5.86 (s, 2H), 7.07 (m, 1H), 7.19-7.49 (m, 4H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 169.49 (quint, J = 19.27 Hz), 146.62, 145.84, 143.81 (sext, J = 5.78 Hz), 126.25, 121.44, 83.51 (m, J = 3.85 Hz), 83.07.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 81.8 (9 lines, A-part), 62.6 (dt, J = 153.03, 3.76 Hz, B$_4$-part).
1-Hydroxy-2-pentafluorosulfanyl-naphthalene (5):

The starting olefin 3 (0.26g, 0.96mmol) was dissolved in 2mL methanol and two drops of hydrochloric acid was added. The reaction mixture was first stirred at 50°C for 3 d and then stirred at 70°C for another 2 d. Water was added to the reaction mixture and it was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated and the pure product was obtained by column chromatography (hexane). (yield: 40%)

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 6.77\) (s, 1H), 7.40 (d, 1H, \(J = 9.17\) Hz), 7.59 (m, 3H), 7.79 (d, \(J = 8.02\) Hz, 1H), 8.41 (d, 1H, \(J = 8.48\) Hz).

\(^{13}\)C-NMR (101 MHz, CDCl\(_3\)): \(\delta = 147.07, 135.34, 135.34\) (m), 129.23, 127.31, 126.73, 125.79, 124.02, 122.85 (m), 120.07.

\(^{19}\)F-NMR (376 MHz, CDCl\(_3\)): \(\delta = 81.89\) (9 lines, A-part), 59.34 (dm, \(J = 148.89\) Hz, \(B_4\)-part).

Crystallographic data:
Table 12: Crystal structure information of 5.

<table>
<thead>
<tr>
<th>Name</th>
<th>1-hydroxy-2-pentafluorosulfanyl-naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>( \text{C}<em>{20}\text{H}</em>{14}\text{F}<em>{10}\text{O}</em>{2}\text{S}_{2} )</td>
</tr>
<tr>
<td>Space group</td>
<td>( P2_1/c )</td>
</tr>
<tr>
<td>Cell Length</td>
<td>( a = 6.337(3); b = 10.385(5); c = 15.832(8) )</td>
</tr>
<tr>
<td>Cell Angles</td>
<td>( a = 96.304(11); b = 90.560(11); g = 99.260(11) )</td>
</tr>
<tr>
<td>Cell Volume</td>
<td>1021.7</td>
</tr>
<tr>
<td>( Z, Z' )</td>
<td>( Z: 2, Z': 0 )</td>
</tr>
<tr>
<td>R-Factor (%)</td>
<td>7.3</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>room temperature (283-303)</td>
</tr>
<tr>
<td>Color</td>
<td>colorless</td>
</tr>
<tr>
<td>Density</td>
<td>1.757</td>
</tr>
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</table>

Table 13: Bond lengths of 5.

<table>
<thead>
<tr>
<th>Atom1</th>
<th>Atom2</th>
<th>Length</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>C1</td>
<td>1.795(8)</td>
</tr>
<tr>
<td>S1</td>
<td>F1</td>
<td>1.596(5)</td>
</tr>
<tr>
<td>S1</td>
<td>F2</td>
<td>1.578(5)</td>
</tr>
<tr>
<td>S1</td>
<td>F3</td>
<td>1.579(6)</td>
</tr>
<tr>
<td>S1</td>
<td>F4</td>
<td>1.593(5)</td>
</tr>
<tr>
<td>S1</td>
<td>F5</td>
<td>1.597(6)</td>
</tr>
<tr>
<td>C1</td>
<td>C2</td>
<td>1.47(1)</td>
</tr>
<tr>
<td>C1</td>
<td>C10</td>
<td>1.33(1)</td>
</tr>
<tr>
<td>C2</td>
<td>H2A</td>
<td>0.93(1)</td>
</tr>
<tr>
<td>C2</td>
<td>C3</td>
<td>1.34(1)</td>
</tr>
<tr>
<td>C3</td>
<td>H3A</td>
<td>0.93(1)</td>
</tr>
<tr>
<td>C3</td>
<td>C4</td>
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</tr>
<tr>
<td>C4</td>
<td>C5</td>
<td>1.48(1)</td>
</tr>
<tr>
<td>C4</td>
<td>C9</td>
<td>1.41(1)</td>
</tr>
<tr>
<td>C5</td>
<td>H5A</td>
<td>0.93(1)</td>
</tr>
<tr>
<td>C5</td>
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Table 14: Angles of 5.

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1,4-Dihydro-2-trifluoromethyl-3-iodo-1,4-epoxynaphtalene (6):

![6](image)

The starting compound 1 (1.0 g, 6.9 mmol) was dissolved in 40 mL of a mixture of water and acetonitrile (1:1) in a pressure glass ampoule (150 ml) fitted with a Rotaflo® valve and magnetic stirring bar and 1 eq of sodium
dithionite and 2 eq sodium phosphate were added. The reaction mixture was cooled down using liquid nitrogen and 1.5 eq of the CF$_3$I was condensed into it. After warming up to room temperature, the mixture was stirred for 6 days. Then water was added, the reaction mixture was extracted with dichloromethane and the combined extract was dried over Na$_2$SO$_4$. The crude product obtained after evaporation of the solvent was subjected to column chromatography (hexanes) to give the pure product. (yield: 92%)

$^1$H-NMR (400 MHz, CDCl$_3$): δ = 7.24 (s, 4H), 5.62 (d, 1H, J = 4.4 Hz), 5.31 (d, 1H, J = 4.4 Hz), 4.00 (t, 1H, J = 4.4 Hz), 2.78-2.72 (m, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): δ = 142.59, 126.58, 123.12, 81.24, 38.72, 49.94 (quar, J = 26.97 Hz), 21.75.

$^{19}$F-NMR (376 MHz, CDCl$_3$): δ = -67.40 (s, 3F).

1,4-Dihydro-2-trifluoromethyl-1,4-epoxynaphtalene (7):

The olefin 6 (1.95 g, 5.7 mmol) was dissolved in 2mL DMSO and 0.34 g (5 eq) of LiOH was added. The mixture was stirred for 12 h at 60 °C. Water was added and the mixture was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated to obtain the pure product. (yield: 64%)

$^1$H-NMR (400 MHz, CDCl$_3$): δ = 7.40-7.19 (m, 4H), 7.05-7.02 (m, 2H), 5.84 (s, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): δ = 150.69, 136.17, 128.55, 122.80, 121.07, 83.22, 81.28.

$^{19}$F-NMR (376 MHz, CDCl$_3$): δ = -64.82 (s, 3F).
1-Hydroxy-2-trifluoromethyl-naphthalene (8)\textsuperscript{[87]}:

\begin{center}
\includegraphics[width=0.2\textwidth]{8}
\end{center}

The starting olefin 7 (0.25 g, 1.17 mmol) was dissolved in 3 mL methanol and six drops of hydrochloric acid was added. The reaction mixture was stirred at 65°C for 15 h. Water was added to the reaction mixture and it was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated and the pure product was obtained by column chromatography (hexane). (yield: 41%)

\begin{align*}
\textsuperscript{1}H-NMR (400 MHz, CDCl}_3: & \delta = 8.24-8.20 (m, 2H), 7.92-7.90 (m, 1H), 7.61-7.55 (m, 2H), 7.45 (d, 1H, J= 1.38 Hz), 5.80 (s, 1H). \\
\textsuperscript{19}F-NMR (376 MHz, CDCl}_3: & \delta = -57.87 (s, 3F).
\end{align*}

5-Chloro-6-pentafluorosulfanyl-7-oxabicyclo[2.2.1] hept-5-ene-2,3-dicarboxylic anhydride (12):

\begin{center}
\includegraphics[width=0.2\textwidth]{12}
\end{center}

In a 3-necked flask equipped with a dry ice condenser and an argon inlet, the olefin 10 (1.00 g, 6.00 mmol) was dissolved in 20 mL anhyd. dichloromethane and cooled down to using liquid nitrogen. Then 3.5 eq SF\textsubscript{5}Cl was condensed into the solution and after warming up to -40°C, 0.03 eq BEt\textsubscript{3} was added slowly, using a syringe. The solution was stirred for 7 h and then warmed up
to ambient temperature. The solvent was evaporated and the pure product was isolated by column chromatography. (yield: 56%)

\[ ^{1}H\text{-NMR (400 MHz, CDCl}_{3}\]: \( \delta = 3.44 \text{ (d, 1H, } J = 8.0 \text{ Hz), 3.94 \text{ (m, 1H, } J_{FH} = 6.0, J_{HH} = 4.0 \text{ Hz), 4.02 \text{ (d, 1H, } J = 8.0 \text{ Hz), 4.85 \text{ (t, 1H, } J = 4.0 \text{ Hz), 5.18 \text{ (d, 1H, } J = 6 \text{ Hz), 5.57 \text{ (s, 1H).}}\]

\[ ^{13}C\text{-NMR (101 MHz, DMSO-d6): } \delta = 172.2, 171.5, 93.33 \text{ (m), 83.22 (quint, } J = 4.5 \text{ Hz), 82.21, 59.61 \text{ (m), 50.57, 45.18.}}\]

\[ ^{19}F\text{-NMR (376 MHz, CDCl}_{3}\]: \( \delta = 80.52 \text{ (9 lines, A-part), 60.46 \text{ (dd, } J_{FF} = 145.0, J_{FH} = 6.0 \text{ Hz, B}_{4}\text{-part).}}\]

6- Pentafluorosulfanyl-dimethyl-7-oxanorbornene-2,3-dicarboxylate (13):

![Image of chemical structure]

The olefin 12 (0.60 g, 1.80 mmol) was dissolved in 5 mL methanol and a catalytic amount of H\(_2\)SO\(_4\) was added. The mixture was stirred for 12 h at ambient temperature, water was added and the mixture was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated to obtain the pure product. (yield: 90%)

\[ ^{1}H\text{-NMR (400 MHz, CDCl}_{3}\]: \( \delta = 3.17 \text{ (d, 1H, } J = 10,0 \text{ Hz), 3.74 \text{ (s, 2H), 3.79 \text{ (d, 1H, } J = 10,0 \text{ Hz), 3.88 \text{ (m, 1H, } J_{FH} = 6.0 \text{ Hz), 4.76 \text{ (m, 1H, } J = 6.0 \text{ Hz), 5.06 \text{ (d, 1H, } J = 6.0 \text{ Hz), 5.40 \text{ (s, 1H).}}\]

\[ ^{13}C\text{-NMR (101 MHz, CDCl}_{3}\]: \( \delta = 170.44, 169.76, 93.39 \text{ (quint, } J = 12.5 \text{ Hz), 83.14 \text{ (quint, } J = 4.0 \text{ Hz), 81.93, 58.07 \text{ (quint, } J = 4.0 \text{ Hz), 51.41, 45.43.}}\]

\[ ^{19}F\text{-NMR (376 MHz, CDCl}_{3}\]: \( \delta = 81.73 \text{ (9 lines, A-part), 59.44 \text{ (dd, } J_{FF} = 135.36, J_{FH} = 6.0 \text{ Hz, B}_{4}\text{-part).}}\]
**Experimental Part**

*Dimethyl 5-chloro-3-oxatricyclo[2.2.1]heptane-1,7-dicarboxylate (15):*

![Formula 15]

The olefin 13 (0.10 g, 0.20 mmol) was dissolved in 2 mL DMSO and 32 mg (5 eq) of LiOH was added. The mixture was stirred for 12 h at 60 °C. Water was added and the mixture was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated to obtain the pure product. (yield: 53%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$= 4.66 (d, 1H, $J = 3.9$ Hz), 4.34 (m, 1H), 4.01 (t, 1H, $J = 2.1$ Hz), 3.73 (s, 3H), 3.71 (s, 3H), 3.67 (s, 1H), 2.35 (ddd, 1H, $J = 3.9$, 1.4, 0.8 Hz).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$= 169.8, 169.0, 78.0, 61.4, 59.3, 52.4, 52.29, 46.7, 29.2.

*Preparation of dimethyl 5-iodo-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate (16):*

![Formula 16]

The starting compound 11 (1.95 g, 9.20 mmol) was dissolved in 80 mL of a mixture of water and acetonitrile (1:1) in a pressure glass ampoule (150 ml) fitted with a Rotaflo$^\circledR$ valve and magnetic stirring bar and 1 eq of sodium dithionite and 2 eq sodium phosphate were added. The reaction mixture was cooled down using liquid nitrogen and 1.5 eq of the CF$_3$I was condensed into it. After warming up to room temperature, the mixture was stirred for 6 days.
Then water was added, the reaction mixture was extracted with dichloromethane and the combined extracts were dried over Na$_2$SO$_4$. The crude product obtained after evaporation of the solvent was subjected to column chromatography (hexanes) to give the pure product. (yield: 65%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta =$ 4.92 (d, 1H, $J =$ 5.04 Hz), 4.90 (s, 1H), 4.00 (t, 1H, $J =$ 5.04 Hz), 3.91 (d, 1H, $J =$ 9.62 Hz), 3.70 (s, 6H), 3.05 (d, 1H, $J =$ 9.62 Hz), 2.58-2.48 (m, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta =$ 170.51, 169.75, 127.00, 124.23, 82.28, 78.66, 57.76 (quart, $J =$ 28.75 Hz), 52.62, 51.34, 49.52, 15.17.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta =$ -70.29 (d, 3F, $J =$ 8.67).

Dimethyl 4-(trifluoromethyl)phthalate (17)$^{[88]}$:

![Dimethyl 4-(trifluoromethyl)phthalate (17)]

The olefin 16 (0.10 g, 0.20 mmol) was dissolved in 2 mL DMSO and 67 mg (2 eq) of K$_2$CO$_3$ was added. The mixture was stirred for 12 h at 60 °C. Water was added and the mixture was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated to obtain the pure product. (yield: 78%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta =$ 8.04-8.00 (m, 1H), 7.81-7.76 (m, 1H), 7.64-7.22 (m, 1H), 3.93 (s, 6H).

$^{19}$F-NMR (101 MHz, CDCl$_3$): $\delta =$ -63.05 (s, 3F).

(1S,2R,3S,4S,5R,6R)-Dimethyl 5-iodo-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate (18):
The starting compound 16 (0.10 g, 0.20 mmol) was dissolved in 2 mL dichloromethane and 0.04 mL (0.04 g, 0.30 mmol) DBU was slowly dropped into the solution. The reaction mixture was stirred at ambient temperature for 12 hours, poured into water and extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated to obtain the pure product. (yield: 72%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$= 4.87 (d, 1H, $J$= 5.5 Hz), 4.77 (d, 1H, $J$= 5.5 Hz), 4.05 (t, 1H, $J$= 5.5 Hz), 3.91 (t, 1H, $J$= 5.95 Hz), 3.78 (s, 6H), 3.54 (t, 1H, $J$= 5.95 Hz), 2.70-2.59 (m, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$= 171.85, 169.63, 127.29, 124.53, 84.57, 78.27, 53.50, 52.94 (d, $J= 11.5$ Hz), 51.10, 48.22, 15.54.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$= -70.35 (d, 3F, $J= 8.67$ Hz).

Crystallographic data:

### Table 15: Crystal structure information of 18.

| Name | (1S,2R,3S,4S,5R,6R)-Dimethyl 5-iodo-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane-2,3- |
### Experimental Part

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Table 16: Bond lengths of 18.
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Table 17: Angles of 18.

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2-Pentafluorosulfanyl-3-chloro-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1] heptane (21):
In a 3-necked flask equipped with a dry ice condenser and an argon inlet, the olefin 20 (0.82 g, 2.40 mmol) was dissolved in 20 mL anhyd. dichloromethane and cooled down to using liquid nitrogen. Then 2 eq SF\textsubscript{5}Cl was condensed into the solution and after warming up to -40°C, 0.03 eq BEt\textsubscript{3} was added slowly, using a syringe. The solution was stirred for 5-12 h and then warmed up to r. t. The solvent was evaporated and the pure product was isolated by column chromatography. (yield: 96%)

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ = 2.26 (td, 1H, J = 9.62, 5.04 Hz), 2.88 (td, 1H, J = 9.16, 6.21 Hz), 3.22-3.42 (m, 4H), 3.33 (s, 2H), 3.91 (dt, 1H, J = 5.95 Hz), 4.51 (d, 1H, J = 5.04 Hz), 4.68 (t, 1H, J = 5.04 Hz), 4.97 (s, 1H).

\textsuperscript{13}C-NMR (101 MHz, CDCl\textsubscript{3}): δ = 94.55 (quint, J = 10.54 Hz), 83.57 (quint, J = 4.00 Hz), 82.24, 69.61, 69.74, 58.96, 58.85, 58.59, 45.91, 38.06.

\textsuperscript{19}F-NMR (376 MHz, CDCl\textsubscript{3}): δ = 83.5 (9 lines, A-part), 59.61 (dt, J = 145.94, 5.78 Hz, B\textsubscript{4}-part).

2-Pentafluorosulfanyl-5,6-bis-methoxymethyl-7-oxabicyclo[2.2.1]hept-2-ene (22):

The olefin 21 (0.13 g, 0.04 mmol) was dissolved in DMSO and 5 eq of LiOH were added. The mixture was stirred for 12 h at 60 °C. Water was added and the mixture was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated to obtain the pure product. (yield: 81%)

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Experimental Part

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$= 2.06 (m, 1H, $J$= 8.25, 5.04 Hz), 2.24 (m, 1H, $J$= 9.01, 5.96 Hz), 3.25-3.53 (m, 4H), 3.33 (s, 2H), 4.96 (s, 1H), 5.03 (s, 1H), 6.71 (d, 1H, $J$= 1.38 Hz).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$= 160.05 (quint, $J$= 19.17, 17.15 Hz), 136.92 (quint, $J$= 5.75), 81.62, 81.43, 71.0, 70.98, 58.83, 58.99, 39.78.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$= 82.33 (9 lines, A-part), 66.64 (d, $J$= 151.72 Hz, B$_4$-part).

$f$ 4-(Pentafluorosulfanyl)benzyl acetate (23):

The starting compound 22 (0.20 g, 0.60 mmol) was dissolved in 3 mL of a mixture of CH$_3$CO$_2$H/H$_2$SO$_4$ (5:1) and heated to 100°C for 24 h. The reaction mixture was poured into water and extracted with dichloromethane. After drying over sodium sulfate, the solvent was removed under vacuum and the product 23 was obtained. (yield: 29%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$= 7.74 (d, 2H, $J$= 8.7 Hz), 7.44 (d, 2H, $J$= 8.7 Hz), 5.18 (s, 2H), 2.13 (s, 3H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$= 170.8, 139.9, 128.1, 126.3 (quint, $J$= 4.7 Hz), 64.9, 20.9.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$= 83.5-85.1 (9 lines, A-part), 62.9 (d, $J$= 149.55.0 Hz, B$_4$-part).

5-(Pentafluorosulfanyl)-1,3-dihydroisobenzofuran (24):
The starting olefin 22 (0.15 g, 0.50 mmol) was dissolved in 2 mL methanol and one drop of hydrochloric acid was added. The reaction mixture was stirred at 100°C for 90 h. The reaction mixture was poured into water and extracted with dichloromethane. After drying over sodium sulfate, the solvent was removed under vacuum and the product 24 was obtained. (yield: 56%)

^1^H NMR (400 MHz, CDCl$_3$): δ= 7.67 (dd, 1H, J = 8.3, 1.8 Hz), 7.62 (s, 1H), 7.31 (d, 1H, J = 8.3 Hz), 5.14 (s, 4H).

^13^C NMR ((101 MHz, CDCl$_3$): δ= 153.6 (quintd, J = 17.3 Hz, 1.2 Hz), 142.9, 140.2, 125.4 (quint, J = 4.7 Hz), 121.2, 119.1 (quint, J = 4.6 Hz), 73.3, 73.2.

^19^F NMR (376 MHz, CDCl$_3$): δ= 84.8 (9 lines, A-part), 63.7 (d, J = 150.0 Hz, B$_4$-part).

Crystallographic data:
Table 18: Crystal structure information of 24.

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<th>Name</th>
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Table 19: Bond lengths of 24.

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2,3-Bis(chloromethyl)-5-(pentfluorosulfanyl)-7-oxabicyclo[2.2.1]hept-5-ene (25):

The starting olefin 22 (0.15 g, 0.50 mmol) was dissolved in 2 mL methanol and one drop of hydrochloric acid was added. The reaction mixture was
stirred at 100°C for 90 h. the reaction mixture was poured into water and extracted with dichloromethane. After drying over sodium sulfate, the solvent was removed under vacuum and the product 25 was obtained. (yield: 11%)

\[ ^1H-NMR \ (400 \text{ MHz, CDCl}_3): \delta = 7.25 \ (s, \ 1H), \ 4.11-4.07 \ (m, \ 2H), \ 3.59-3.52 \ (m, \ 4H), \ 2.79-2.84 \ (m, \ 2H). \]

\[ ^{13}C-NMR \ (101 \text{ MHz, CDCl}_3): \delta = 127.5 \ (t, \ J= 150.3 \text{ Hz}), \ 74.80, \ 60.88, \ 56.33, \ 45.24, \ 43.34, \ 42.38. \]

\[ ^{19}F-NMR \ (376 \text{ MHz, CDCl}_3): \delta = 81.25-82.85 \ (9 \text{ lines, A-part}), \ 59.10 \ (d, \ J= 150.28 \text{ Hz, B}_4\text{-part}). \]

2-iodo-5,6-bis(methoxymethyl)-3-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane (28):

The starting compound 20 (1.31 g, 7.10 mmol) was dissolved in 60 mL of a mixture of water and acetonitrile (1:1) in a pressure glass ampoule (150 ml) fitted with a Rotaflo® valve and magnetic stirring bar and 1 eq of sodium dithionite and 2 eq sodium phosphate were added. The reaction mixture was cooled down using liquid nitrogen and 1.5 eq of the CF3I was condensed into it. After warming up to room temperature, the mixture was stirred for 6 days. Then water was added, the reaction mixture was extracted with dichloromethane and the combined extracts were dried over Na2SO4. The crude product obtained after evaporation of the solvent was subjected to column chromatography (hexanes) to give the pure product. (yield: 65%)

\[ ^1H-NMR \ (400 \text{ MHz, CDCl}_3): \delta = 4.43 \ (s, \ 1H), \ 4.33 \ (d, \ 1H, \ J= 4.58 \text{ Hz}), \ 3.92 \ (t, \ 1H, \ J= 5.5 \text{ Hz}), \ 3.29 \ (s, \ 6H), \ 3.27 \ (s, \ 4H), \ 3.02-2.95 \ (m, \ 1H), \ 2.55-2.47 \ (m, \ 1H), \ 2.16-2.09 \ (m, \ 1H). \]
Experimental Part

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 126.23 (quart, $J$ = 278.9 Hz), 82.82, 70.24, 69.54, 58.86 (d, $J$ = 11.5 Hz), 57.84 (quart, $J$ = 27.8 Hz), 46.01, 42.33, 17.32.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = -70.32 (d, $J$ = 8.67 Hz).

2,3-Bis(methoxymethyl)-5-(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-5-ene (29):

![Chemical Structure](image)

The olefin 28 (1.15 g, 3.00 mmol) was dissolved in 5mL DMSO and 0.36g (5 eq) of LiOH was added. The mixture was stirred for 12 h at 60°C. Water was added and the mixture was extracted with dichloromethane. After drying with sodium sulfate, the solvent was evaporated to obtain the pure product. (yield: 75%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 6.75 (s, 1H), 4.97 (s, 1H), 4.96 (s, 1H), 3.54-3.49 (m, 1H), 3.48-3.42 (m, 1H), 3.36 (s, 4H), 3.35 (s, 6H), 2.11-2.04 (m, 1H), 2.03-1.96 (m, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 139.0-138.6 (m), 122.03 (quart, $J$ = 268.37 Hz), 81.62, 79.35, 77.17 (t, $J$ = 32.6 Hz), 71.18 (d, $J$ = 5.8 Hz), 58.83 (d, $J$ = 13.4 Hz), 40.02, 39.79.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = -63.55 (s, 3F).
E.2 Preparation of SF₅-containing aromatics via arylsulfur chlorotetrafluorides

*Phenylsulfur chlorotetrafluoride (32)*\(^{[47]}\):

![Chemical Structure of Phenylsulfur Chlorotetrafluoride](image)

To a solution of 31 (16.50 g, 75.50 mmol) in dry acetonitrile (2.8M) spray-dried KF (16 eq) was added. The mixture was with an ice bath and chlorine was introduced into the solution. After several hours the temperature of the reaction mixture was allowed to reach room temperature and the color of the mixture changed from yellow to white. After 8 h of passing chlorine the mixture was yellow again. At this point the chloride bubbling was stopped and the mixture was stirred for another 12 h. The solid was removed by filtration, and washed with hexane. The product was distilled under reduced pressure and stored in a fluoropolymer container at 2–8°C. (yield: 89%)

\(^1\)H-NMR (400 MHz, CDCl₃): \(\delta = 7.75–7.72 \text{ (m, 2H), 7.49–7.42 \text{ (m, 3H)}}\).

\(^19\)F-NMR (101 MHz, CDCl₃): \(\delta = 137.3 \text{ (s, 4F)}}\).

*Phenylsulfur pentafluoride (33)*\(^{[47]}\):

![Chemical Structure of Phenylsulfur Pentafluoride](image)
To a stirred solution of 32 (3.88 g, 19.00 mmol) in TFA (0.1M) in a fluoropolymer screw-cap flask, KHF$_2$ was added (0.6 eq in two portions every 15 min). The reaction mixture was stirred at room temperature for 20 h, and then poured into water. Extraction into dichloromethane, drying (Na$_2$SO$_4$), and solvent removal provided the crude product which was purified by chromatography on silica gel using hexane as eluent giving pure 33. (yield: 82%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.78–7.74 (m, 2H), 7.53–7.44 (m, 3H).

$^{19}$F-NMR (176 MHz, CDCl$_3$): $\delta$ = 85.5–83.8 (m, 1F), 62.7 (d, 4F, $J$ = 150.3 Hz).

4-Fluorophenylsulfur chlorotetrafluoride (35)$^{[47]}$:

![Image of 4-Fluorophenylsulfur chlorotetrafluoride](image)

To a solution of 34 (9.27 g, 36.40 mmol) in dry acetonitrile (2.8M) spray-dried KF (16 eq) was added. The mixture was with an ice bath and chlorine was introduced into the solution. After several hours the temperature of the reaction mixture was allowed to reach room temperature and the color of the mixture changed from yellow to white. After 8 h of passing chlorine the mixture was yellow again. At this point the chloride bubbling was stopped and the mixture was stirred for another 12 h. The solid was removed by filtration, and washed with hexane. The product was distilled under reduced pressure and stored in a fluoropolymer container at 2–8°C. (yield: 86%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.74 (m, 2H), 7.11 (m, 2H).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 138.3 (s, 4F), -107.0 (s, 1F).
**4-Fluorophenylsulfur pentafluoride (36)**[^47]:

![Diagram of 4-Fluorophenylsulfur pentafluoride (36)]

To a stirred solution of 35 (3.11 g, 14.00 mmol) in TFA (1M) in a fluoropolymer screw-cap flask, KHF$_2$ was added (0.6 eq in two portions every 15 min). The reaction mixture was stirred at room temperature for 18 h, and then poured into water. Extraction into dichloromethane, drying (Na$_2$SO$_4$), and solvent removal provided the crude product which was purified by chromatography on silica gel using hexane as eluent giving pure 36. (yield: 69%)

$^1$H-NMR (400 MHz, CDCl$_3$): δ = 7.76 (m, 2H), 7.13 (t, 2H, J = 8.4 Hz).
$^{19}$F-NMR (376 MHz, CDCl$_3$): δ = 85.1–83.5 (m, 1F), 63.8 (d, 4F, J = 150.3 Hz), -107.1 (m).

**4-Chlorophenylsulfur chlorotetrafluoride (38)**[^47]:

![Diagram of 4-Chlorophenylsulfur chlorotetrafluoride (38)]

To a solution of 37 (10 g, 34.80 mmol) in dry acetonitrile (2.8M) spray-dried KF (16 eq) was added. The mixture was with an ice bath and chlorine was introduced into the solution. After several hours the temperature of the reaction mixture was allowed to reach room temperature and the color of the mixture changed from yellow to white. After 8 h of passing chlorine the
mixture was yellow again. At this point the chloride bubbling was stopped and the mixture was stirred for another 12 h. The solid was removed by filtration, and washed with hexane. The product was distilled under reduced pressure and stored in a fluoropolymer container at 2–8 °C. (yield: 81%)

$$^1$$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.67 (dm, 2H, $J$ = 9.2 Hz), 7.42 (d, 2H, $J$ = 9.2 Hz);
$$^{19}$$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 137.4 (s, 4F).

4-Chlorophenylsulfur pentafluoride (39)$^{[a7]}$:

To a stirred solution of 38 (7.87 g, 33.00 mmol) in TFA (1.1M) in a fluoropolymer screw-cap flask, KHF$_2$ was added (0.66 eq in two portions every 30 min). The reaction mixture was stirred at room temperature for 12 h, and then poured into water. Extraction into dichloromethane, drying (Na$_2$SO$_4$), and solvent removal provided the crude product which was purified by chromatography on silica gel using hexane as eluent giving pure 39. (yield: 75%)

$$^1$$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.69 (dm, 2H, $J$=8.8 Hz), 7.43 (d, 2H, $J$ = 8.8 Hz).
$$^{19}$$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 84.5–82.9 (m, 1F), 63.3 (d, 4F, $J$ = 150.3 Hz).
4-(tert-Butyl)phenylsulfur chlorotetrafluoride (41):  

![Chemical Structure](image)

To a solution of 40 (14.84 g, 89.30 mmol) in dry acetonitrile (2.8M) spray-dried KF (16 eq) was added. The mixture was with an ice bath and chlorine was introduced into the solution. After several hours the temperature of the reaction mixture was allowed to reach room temperature and the color of the mixture changed from yellow to white. After 8 h of passing chlorine the mixture was yellow again. At this point the chloride bubbling was stopped and the mixture was stirred for another 12 h. The solid was removed by filtration, and washed with hexane. The product was recrystallized from hexane and stored in a fluoropolymer container at 2‒8°C. (yield: 55%)

\(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta=7.65\) (dm, 2H, \(J = 8.7\) Hz), \(7.43\) (d, 2H, \(J = 8.7\) Hz), \(1.32\) (s, 9H).
\(^19\)F-NMR (376 MHz, CDCl\(_3\)): \(\delta=138.3\) (s, 4F).

4-(tert-Butyl)phenylsulfur pentafluoride (42):

![Chemical Structure](image)

To a stirred solution of 41 (4.95 g, 19.00 mmol) in TFA (0.76M) in a fluoropolymer screw-cap flask, KHF\(_2\) was added (0.66 eq two portions every
30 min). The reaction mixture was stirred at room temperature for 12 h, and then poured into water. Extraction into dichloromethane, drying (Na$_2$SO$_4$), and solvent removal provided the crude product which was purified by chromatography on silica gel using hexane as eluent giving pure 42. (yield: 54%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.70 (dm, 2H, $J = 8.7$ Hz), 7.48 (dm, 2H, $J = 8.7$ Hz), 1.34 (s, 9H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 155.1, 151.5 (quin, $J = 16.3$), 125.7, 35.0, 31.1 (s, 3C).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 86.3–84.7 (m, 1F), 63.3 (d, 4F, $J = 150.3$ Hz).

HRMS (Cl) m/z calcd for C$_{10}$H$_{13}$F$_5$S [M]$^+$ 260.0658, found 260.0650.

2,4-Difluorophenylsulfur chlorotetrafluoride (44):

![Diagram of 2,4-Difluorophenylsulfur chlorotetrafluoride](image)

To a solution of 43 (12.60 g, 43.40 mmol) in dry acetonitrile (2.8M) spray-dried KF (16 eq) was added. The mixture was with an ice bath and chlorine was introduced into the solution. After several hours the temperature of the reaction mixture was allowed to reach room temperature and the color of the mixture changed from yellow to white. After 8 h of passing chlorine the mixture was yellow again. At this point the chloride bubbling was stopped and the mixture was stirred for another 12 h. The solid was removed by filtration, and washed with hexane. The product was distilled under reduced pressure and stored in a fluoropolymer container at 2–8°C. (yield: 63%)
$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.78–7.70 (m, 1H), 6.97–6.87 (m, 2H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 164.4 (dd, $J = 258.8$, 12.5 Hz), 156.8 (dd, $J = 263.6$, 12.5 Hz), 137.8 (quindd, 1C, $J = 11.5$, 4.2), 130.0 (m), 111.4 (d, $J = 22.0$ Hz), 105.7 (t, $J = 26.8$ Hz).

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 141.4 (m, 4F), –102.1 to –102.5 (m, 1F), –102.5 to –102.7 (m, 1F).


2,4-Difluorophenylsulfur pentafluoride (45):

![45]

To a stirred solution of 44 (0.91g, 3.80 mmol) in TFA (0.3M) in a fluoropolymer screw-cap flask, KHF$_2$ was added (1 eq followed by 2 equiv. after 1 h). The reaction mixture was stirred at 50 °C for 12 h, and then poured into water. Extraction into dichloromethane, drying (Na$_2$SO$_4$), and solvent removal provided the crude product, which was purified by treatment with NAOH in water and extraction with giving pure 45. (yield: 14%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.77 (ddd, 1H, $J = 9.2$, 7.8, 5.7 Hz), 7.01–6.97 (m, 1H), 6.97–6.93 (m, 1H).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 164.4 (dd, $J = 244.5$, 13.6 Hz), 157.1 (ddquint, $J = 262.5$, 11.7, 1.6 Hz), 136.5 (quintdd, $J = 15.9$, 4.5, 1.2 Hz), 130.2 (m,), 111.6 (dd, $J = 22.5$, 3.7 Hz), 105.8 (t, $J = 26.5$ Hz).
Experimental Part

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 81.9–80.3 (m, 1F), 68.6 (dd, 4F, $J$ = 151.4, 25.3 Hz), −102.8 to −102.9 (m, 1F), −102.9 to −103.2 (m, 1F).

HRMS (CI) $m/z$ calcd for C$_{6}$H$_{3}$F$_{7}$S [M]$^+$ 239.9844, found 239.9842.

4-(4-Propylcyclohexyl)phenylsulfur chlorotetrafluoride (47):

To a solution of 46 (10.00 g, 21.40 mmol) in dry acetonitrile (2.8M) spray-dried KF (16 eq) was added. The mixture was with an ice bath and chlorine was introduced into the solution. After several hours the temperature of the reaction mixture was allowed to reach room temperature and the color of the mixture changed from yellow to white. After 8 h of passing chlorine the mixture was yellow again. At this point the chlorine bubbling was stopped and the mixture was stirred for another 12 h. The solid was removed by filtration, and washed with hexane. The product was stored in a fluoropolymer container at 2–8°C. (yield: 84%)

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 7.64 (d, 2H, $J$=8.2 Hz), 7.26 (d, 2H, $J$ = 8.2 Hz), 2.52 (tm, 1H, $J$= 11.9 Hz), 1.88 (d, 4H, $J$ = 11.0 Hz), 1.51-1.19 (m, 7H), 1.11–1.01 (m, 2H), 0.91 (t, 3H, $J$ = 7.3 Hz).

$^{13}$C-NMR (101 MHz, CDCl$_3$): $\delta$ = 153.3 (quint, $J$ = 17.3 Hz), 152.0, 127.1, 125.8, 44.4, 39.7, 37.1, 34.0, 33.4, 20.1, 14.5.

$^{19}$F-NMR (376 MHz, CDCl$_3$): $\delta$ = 138.4 (s).

Anal. Calcd for C$_{15}$H$_{21}$ClF$_4$S: C, 52.24; H, 6.15. Found: C, 52.43; H, 6.28.
4-(4-Propylcyclohexyl)phenylsulfur pentafluoride (48)\textsuperscript{18}:

![48](image)

To a stirred solution of 47 (0.62 g, 1.90 mmol) in TFA (0.21M) in a fluoropolymer screw-cap flask, KHF\textsubscript{2} was added (1 eq followed by 2 eq after 1 h). The reaction mixture was stirred at room temperature for 18 h, and then poured into water. Extraction with dichloromethane, drying with Na\textsubscript{2}SO\textsubscript{4} and solvent removal provided 48. (yield: 79%)

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): δ = 7.64 (dm, 2H, J = 8.7 Hz), 7.26 (dm, 2H, J = 8.7 Hz), 2.51 (t, 1H, J = 12.3 Hz), 1.87 (m, 4H), 1.49–1.16 (m, 7H), 1.10–0.98 (m, 2H), 0.89 (t, 3H, J = 7.3 Hz).

\textsuperscript{19}F-NMR (376 MHz, CDCl\textsubscript{3}): δ = 86.4–84.8 (m, 1F), 63.0 (d, 4F, J = 150.3 Hz).

Recovery and reuse of TFA in the synthesis of 48:

KHF\textsubscript{2} (492 mg, 6.3 mmol) was added to a solution of 47 (2.17 g, 6.30 mmol) in TFA (21 mL) in a fluoropolymer flask. The mixture was stirred at room temperature and after 1 h, KHF\textsubscript{2} (984 mg, 12.6 mmol) was added. The mixture was stirred for further 17 h and then transferred to a glass round bottom flask. The solvent was distilled under normal pressure (90°C bath temperature). Water was added to the residue and the product was worked-up as described above giving 48 (71% yield, 1.47 g). To a solution of 47 (0.76 g, 2.20 mmol) in recovered TFA (7.4 mL), KHF\textsubscript{2} (172 mg, 2.2 mmol) was added. The mixture was stirred at room temperature for 1 h followed by addition of KHF\textsubscript{2} (343 mg, 4.4 mmol). The mixture was stirred for further 17 h, followed by addition of water and work-up as described above giving 48 (63% yield, 455 mg). To a solution of 47 (0.59 g, 1.7 mmol) in recovered TFA (5.8 mL), KHF\textsubscript{2} (134 mg, 1.7 mmol) was added. The mixture was stirred at room temperature for 1 h.
followed by addition of KHF$_2$ (268 mg, 3.4 mmol). The mixture was stirred for further 17 h, followed by addition of water and work-up as described above giving 48 (70% yield, 391 mg).
### F.1 List of new compounds

Table 21: List of new compounds.

<table>
<thead>
<tr>
<th>No.</th>
<th>name</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1,4-dihydro-2-pentafluorosulfanyl-3-chloro-1,4-epoxynaphtalene</td>
<td><img src="image1.png" alt="Structure 1" /></td>
</tr>
<tr>
<td>3</td>
<td>1,4-dihydro-2-pentafluorosulfanyl-1,4-epoxynaphtalene</td>
<td><img src="image2.png" alt="Structure 2" /></td>
</tr>
<tr>
<td>5</td>
<td>1-hydroxy-2-pentafluorosulfanyl-naphthalene</td>
<td><img src="image3.png" alt="Structure 3" /></td>
</tr>
<tr>
<td>6</td>
<td>1,4-dihydro-2-trifluoromethyl-3-iodo-1,4-epoxynaphtalene</td>
<td><img src="image4.png" alt="Structure 4" /></td>
</tr>
<tr>
<td>7</td>
<td>1,4-dihydro-2-trifluoromethyl-1,4-epoxynaphtalene</td>
<td><img src="image5.png" alt="Structure 5" /></td>
</tr>
<tr>
<td>12</td>
<td>5-chloro-6- pentafluorosulfanyl-7-oxabicyclo[2.2.1] hept-5-ene-2,3-dicarboxylic anhydride</td>
<td><img src="image6.png" alt="Structure 6" /></td>
</tr>
<tr>
<td>13</td>
<td>6- pentafluorosulfanyl-dimethyl-7-oxanorbornene-2,3-dicarboxylate</td>
<td><img src="image7.png" alt="Structure 7" /></td>
</tr>
<tr>
<td>15</td>
<td>dimethyl 5-chloro-3-oxatricyclo[2.2.1] heptane-1,7-dicarboxylate</td>
<td><img src="image8.png" alt="Structure 8" /></td>
</tr>
<tr>
<td>16</td>
<td>5-iodo-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate</td>
<td><img src="image9.png" alt="Structure 9" /></td>
</tr>
<tr>
<td></td>
<td>Chemical Structure</td>
<td>Formula and Description</td>
</tr>
<tr>
<td>---</td>
<td>-------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>18</td>
<td><img src="image1.png" alt="Image" /></td>
<td>(1S,2R,3S,4S,5R,6R)-dimethyl 5-iodo-6-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylate</td>
</tr>
<tr>
<td>21</td>
<td><img src="image2.png" alt="Image" /></td>
<td>2-pentafluorosulfanyl-3-chloro-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]heptane</td>
</tr>
<tr>
<td>22</td>
<td><img src="image3.png" alt="Image" /></td>
<td>2-pentafluorosulfanyl-5,6-bis-methoxymethyl-7-oxa-bicyclo[2.2.1]hept-2-ene</td>
</tr>
<tr>
<td>23</td>
<td><img src="image4.png" alt="Image" /></td>
<td>4-(pentafluorosulfanyl)benzyl acetate</td>
</tr>
<tr>
<td>24</td>
<td><img src="image5.png" alt="Image" /></td>
<td>5-(pentafluorosulfanyl)-1,3-dihydroisobenzofuran</td>
</tr>
<tr>
<td>25</td>
<td><img src="image6.png" alt="Image" /></td>
<td>2,3-bis(chloromethyl)-5-(pentafluorosulfanyl)-7-oxabicyclo[2.2.1]hept-5-ene</td>
</tr>
<tr>
<td>28</td>
<td><img src="image7.png" alt="Image" /></td>
<td>2-iodo-5,6-bis(methoxymethyl)-3-(trifluoromethyl)-7-oxabicyclo[2.2.1]heptane</td>
</tr>
<tr>
<td>29</td>
<td><img src="image8.png" alt="Image" /></td>
<td>2,3-bis(methoxymethyl)-5-(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-5-ene</td>
</tr>
<tr>
<td>42</td>
<td><img src="image9.png" alt="Image" /></td>
<td>4-(tert-Butyl)phenylsulfur pentafluoride</td>
</tr>
<tr>
<td>44</td>
<td><img src="image10.png" alt="Image" /></td>
<td>2,4-difluorophenylsulfur chlorotetrafluoride</td>
</tr>
<tr>
<td>45</td>
<td><img src="image11.png" alt="Image" /></td>
<td>2,4-difluorophenylsulfur pentafluoride</td>
</tr>
</tbody>
</table>
F.2 Achievements

Application of 7-Oxabicyclo[2.2.1]hept-2-ene derivatives for the synthesis of SF$_5$- and CF$_3$-substituted aromatics
NanoFun Center & NanoMol Graduate Program Retreat, May 2012, Clausthal Zellerfeld, Germany (Oral Presentation)

Application of 7-oxabicyclo[2.2.1]hept-2-ene derivatives for the synthesis of SF$_5$- and CF$_3$-substituted aromatics
Katrin Lummer, Maxim V. Ponomarenko, Yurii A. Serguchev, Gerd-Volker Röschenthaler
20th International Symposium of Fluorine Chemistry, 22-27$^{th}$ July, 2012, Kyoto, Japan (Poster Presentation)

Application of 7-Oxabicyclo[2.2.1]hept-2-enederivatives for the synthesis of SF$_5$- and CF$_3$-substituted aromatics
15. Deutscher Fluortag, 22-24$^{th}$ Sept 2012, Schmitten/Dorfweil, Germany (Oral Presentation)

An improved method for the fluorination of arylsulfur chlorotetrafluorides to arylsulfur pentafluorides
Katrin Lummer, Maxim V. Ponomarenko, Gerd-Volker Röschenthaler, Petr Beier, J. Fluorine Chem., 2013
Paper in progress

Verfahren zur Herstellung von Arylschwefelpentafluoriden,
P. Beier(Institute of Organic Chemistry, Czech Academy of Science, Prague), G.-V. Röschenthaler (Jacobs University Bremen), K. Lummer (Jacobs University Bremen), M. Ponomarenko (Jacobs University Bremen)
DE 10 2013 104 361.1
Synthesis of Novel SF₅- and CF₃-arenes using 7-oxabicyclo[2.2.1]hept-2-ene derivatives
paper in progress
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