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The Synthesis and Characterization of Novel Pentafluorosulfanyl-Containing Heterocycles and Pentafluorosulfanyldifluoromethane

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THE SYNTHESIS AND CHARACTERIZATION OF NOVEL PENTAFLUOROSULFANYL-CONTAINING HETEROCYCLES AND PENTAFLUOROSULFANYLDIFLUOROMETHANE

A Dissertation
Presented to
the Graduate School of
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In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Chemistry

by
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ABSTRACT

Beginning in the early 1960s, scientists began to experiment with the pentafluorosulfanyl moiety. The unique properties of the functional group have attracted interest among fluorine chemists and more recently even organic chemists. These properties include high group electronegativity, high steric bulk, high lipophilicity, a highly electron withdrawing nature, and a square pyramidal geometry. However, the development and deployment of the pentafluorosulfanyl functional group has been significantly slowed. The main cause for the slow development is a lack of easily available reagents to synthesize pentafluorosulfanyl-containing compounds. Historically, the primary reagents used for synthesizing pentafluorosulfanyl-containing compounds were SF₅Cl and SF₅Br. These two compounds are difficult to synthesize, cost prohibitive, and difficult to utilize without a vacuum line. With the development of a convenient, cost-effective synthesis of phenylsulfur pentafluorides, the presence of pentafluorosulfanyl in synthetic chemistry has been increasing.

Starting from SF₅N=CCl₂, a number of five-membered heterocycles have been synthesized. Starting from 1,2-substituted binucleophiles, several classes of heterocycles have been formed, including SF₅N= substituted carbonates, a pentafluorosulfanylimino-substituted benzothiazolinone, and a pentafluorosulfanylimino-substituted benzoxazolinone.

Another aspect of this work depends on a reagent that has recently been synthesized in a reliable, safe and scalable method, namely pentafluorosulfanyldifluoroacetic acid. Pentafluorosulfanyldifluoroacetic acid can be converted to the corresponding acyl chloride by reaction with PCl₅, and subsequently added to the amino group of various 2-amino benzamides. The newly formed 2-pentafluorosulfanyldifluoroacetamido benzamides can then be cyclized to quinazolinones by a dehydration in glacial acetic acid.

From SF₅CF₂I, pentafluorosulfanyldifluoromethane has been synthesized by two reductive methods. The first method utilized by tri-n-butyl tin hydride to produce SF₅CF₂H, at 37% yield. The second method utilized a solution of triethylborane in hexanes, with had a yield of 49% of SF₅CF₂H. Pentafluorosulfanyldifluoromethane was first reported in 1950, though the primary evidence of this discovery was provided in the form of an empirical formula, derived from elemental analysis. Here, a more thorough spectroscopic analysis of the compound is presented, including IR, NMR and Raman spectroscopy.
DEDICATION

Thank you to my parents, Carol and Gary Belina for their support throughout my research. Thank you to my wife, Xiaolin. Her constant encouragement and kindness are a source of inspiration to me. I would like to dedicate this dissertation to her.
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CHAPTER ONE

1.1 Introduction

Currently, the development of pentafluorosulfanyl chemistry is an important branch of fluorine chemistry. The primary aims of research into the SF$_5$ moiety include the development of new methods for synthesizing SF$_5$-containing compounds, as well as developing applications for SF$_5$-containing compounds.\(^1\) Over the past five years, the development of pentafluorosulfanyl-containing compounds with potential applications in pharmaceuticals and electronics has greatly increased.\(^2\) This can be traced to the greater availability of pentafluorosulfanyl-containing benzenes, as in 2009, an improved technique for synthesizing SF$_5$-containing benzenes was patented.\(^3\) This patent has led to the inclusion of SF$_5$ in a greater number of molecules, and with it, new applications for the pentafluorosulfanyl moiety. Pentafluorosulfanyl-containing molecules have been proposed as insecticides, anti-malarial compounds, anti-tuberculosis compounds, and COX-2 inhibitors.\(^4\) Beyond the scope of pharmaceuticals, pentafluorosulfanyl-containing compounds have also been proposed for inclusion in liquid crystalline displays and emissive organometallic complexes.\(^5\)

The unique properties of the pentafluorosulfanyl moiety have driven research into the functional group. One of the important properties of the functional group is its high group electronegativity. This group electronegativity has been measured by several different methods. Using core ionization energies, the group electronegativity has been calculated to be between 2.88 on the Pauling scale for SF$_5$SF$_5$, and 3.03 on the Pauling scale for SF$_5$Cl.\(^6\) A second measurement technique involves the use of $^{13}$C NMR spectroscopy.\(^7\) By measuring the $^{13}$C NMR spectroscopic shifts of SF$_5$-containing sulfonic
acids, the group electronegativity of the pentafluorosulfanyl group was calculated to be 3.62 on the Pauling scale. Though different measurement techniques provide differing values of the electronegativity of the pentafluorosulfanyl group, one can conclude that it has a relatively high group electronegativity.

Another significant property of the pentafluorosulfanyl functional group is its highly electron withdrawing nature. Arylsulfur pentafluorides have a highly meta directing influence with regards to electrophilic aromatic substitution. Measurements based on the ionization of pentafluorosulfanyl-containing aniline, phenol, and benzoic acid derivatives help to illustrate the electron withdrawing nature of the functional group. From the acidity constant of SF$_5$-containing anilinium ions in a weakly acidic buffered solution, the pK$_a$ values for meta-substituted pentafluorosulfanylaniline and para-substituted pentafluorosulfanylaniline were determined to be 2.82 and 2.17, respectively. These values of the SF$_5$-substituted compounds are slightly lower than those of the CF$_3$-substituted anilinium ions, where the pK$_a$ values for the meta- and para-substituted derivatives were 3.20 and 2.75, respectively. The Hammett sigma values for meta-pentafluorosulfanyl benzoic acid and para-pentafluorosulfanyl benzoic acid are 0.61 and 0.68, respectively, as listed in Table 1.1. Another indication of the highly inductive behavior of the pentafluorosulfanyl group comes from the dipole moment of phenylsulfur pentafluoride, with a value of 3.44 Debye.

Another interesting aspect of the SF$_5$ functional group is the molecular geometry of the functional group as illustrated in Figure 1.1. With SF$_5$, the functional group has the shape of a square-based pyramid. The four equatorial fluorine atoms form a square, positioned at approximately 90-degree angles to both the axial fluorine atom and sulfur,
as well as the axial atom bonded to sulfur, be it fluorine, as in sulfur hexafluoride, or another atom.

Table 1.1. A comparison of the Hammett values of the SF₅, CF₃, and SCF₃ functional groups.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>σ_P</th>
<th>σ_I</th>
<th>σ_R</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₅</td>
<td>0.68</td>
<td>0.55</td>
<td>0.11</td>
</tr>
<tr>
<td>CF₃</td>
<td>0.53</td>
<td>0.39</td>
<td>0.12</td>
</tr>
<tr>
<td>SCF₃</td>
<td>0.51</td>
<td>0.31</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The unique shape of the moiety allows for the functional group to fit into biological receptors where other functional groups may not.¹⁰

Figure 1.1. A three-dimensional representation of the pentafluorosulfanyl group.
The volume of the SF$_5$ functional group is considerable as well. Using measurements of the bond angles in SF$_5$CH$_2$SF$_5$ and SF$_5$CF=CF$_2$, the volume of the functional group has been estimated.$^{11}$ With SF$_5$CH$_2$SF$_5$, the bond angle of the S-C-S bond is $126.1(8)^\circ$. For comparison, the C-C-C bond angle in di-$t$-butylmethane is $128^\circ$. From this relatively large S-C-S bond angle, the bulkiness of the SF$_5$ group can be concluded to be slightly less than that of the tert-butyl group. The volume of the SF$_5$ functional group has been shown to be 49.2 cm$^3$/mol.

One of the most useful properties of the SF$_5$ functional group is its high lipophilicity. Lipophilicity refers to the solubility of a compound in non-polar compounds. Measuring the octanol/water partition coefficient of 3-pentafluorosulfanyl phenoxyacetic acid gave a value of 1.51, which is only surpassed by that of the SCF$_3$ functional group.$^{14}$

Some of the applications of SF$_5$-containing compounds include use in pharmaceuticals, agrochemicals, and liquid crystals. In these fields, the pentafluorosulfanyl moiety has gained increasing interest. In several examples, the development of SF$_5$-containing compounds with commercially relevant applications is quite advanced. Describing the most significant advances in the field may further serve to illustrate the utility of research into the pentafluorosulfanyl moiety.

In the field of antimalarial pharmaceutical research, the SF$_5$ moiety has been quite influential in recent years. First, the synthesis of mefloquine with the pentafluorosulfanyl group substituted at the 6-, 7-, or 8- position of the compound has been achieved. Using pentafluorosulfanyl-substituted aniline, the SF$_5$-substituted mefloquine can be produced in a four-step synthesis. The 6-pentafluorosulfanyl and 7-pentafluorosulfanyl mefloquine compounds (Figure 1.2) showed similar or lower IC$_{50}$ values versus mefloquine and the
CF₃-substituted congener against the Plasmodium falciparum parasite.⁴b A second antimalarial compound known as DSM265 and illustrated in Figure 1.3 has shown great promise as well. This compound is based on the triazolopyrimidine scaffold. To synthesize the compound, a five-step synthesis is employed.

![Figures A and B](image.png)

Figure 1.2. Pentafluorosulfanyl-substituted derivatives of Mefloquine.

To add the pentafluorosulfanyl functionality, 4-SF₅ aniline is added to the requisite 7-chloro-triazolopyrimidine. DSM265’s method of malaria inhibition relies on inhibition of the Plasmodium falciparum dihydroorotate dehydrogenase. The enzyme dihydroorotate dehydrogenase is used to catalyze dihydroorotate to orotate, which is part of the synthesis of pyrimidines. Inhibiting this pathway is beneficial, as the malaria parasite is vulnerable to this attack. Plasmodium falciparum lacks other sources of pyrimidine nucleosides present in other organisms. This particular compound is currently undergoing clinical trials in order to test its potential as an antimalarial compound.⁴c,¹⁵

Cyclooxygenases are essential enzymes in the conversion of arachidonic acid to prostaglandins. These compounds have been linked to increased inflammation in the body.
By inhibiting the action of cyclooxygenases, the production of prostaglandin PGH$_2$ and its various metabolites can be reduced, thus reducing inflammation. Cyclooxygenases are found in two forms, COX-1 and COX-2. The inhibition of COX-1 can lead to undesirable side effects, such as bleeding and ulcer formation in the gastrointestinal tract. Selective inhibition of COX-2 is preferable as a treatment for inflammation. The selective addition of pentafluorosulfanyl to benzopyrans has been achieved. The newly formed benzopyran compounds have been investigated for their ability to inhibit COX-2. To synthesize the compounds, p-pentafluoro-sulfanyl phenol was used as a starting material. An aldehyde group was added to the starting material at the ortho position to the hydroxyl group. The compound was then cyclized with ethyl 4,4,4-trifluoro-crotonate and subsequently hydrolyzed in the presence of an aqueous base to give the desired benzopyran. Upon testing in rat models, compound R,S-3a was found to be effective in reducing inflammation and pain (Figure 1.4). Excellent efficacy in the adjuvant-induced arthritis model was found, with an ED$_{50}$ value of 0.094 mg/kg in blocking edema, as well as arthritis. To test the effectiveness of the compound R,S-3a in the adjuvant-induced arthritis model, each rat tested received an injection of adjuvant to the base of the tail. The adjuvant chosen was heat-killed Mycobacterium tuberculosis in mineral oil.
Liquid crystals were first identified in 1888.\textsuperscript{17} Cholesteryl benzoate, when heated above its melting point, displays some properties of both a crystal and a liquid. Liquid crystals are used today in display applications, such as televisions and computer monitors, i.e., LCDs. Improvements in liquid crystalline technology will allow for these displays to have faster refresh rates. A requirement of liquid crystals to be used in active matrix type displays, such as televisions, is a high dielectric anisotropy. The large dipole moment of the pentafluorosulfanyl group makes it an ideal candidate for inclusion in liquid crystals. Several liquid crystalline compounds have been prepared with the pentafluorosulfanyl moiety to this end (Figure 1.5).\textsuperscript{5b} The inclusion of the SF\textsubscript{5} moiety to these compounds increased the dielectric anisotropy of the compounds versus their trifluoromethyl-containing counterparts.

![Figure 1.4. The structure of model compound R,S-3a.](image)

![Figure 1.5. Examples of liquid crystals that contain the pentafluorosulfanyl moiety.](image)
With the sudden increase in interest in SF$_5$-benzenes, a prudent research angle would be to increase the ability for researchers to utilize the pentafluorosulfanyl moiety. To that end, explorations into the SF$_5$N- and SF$_5$CF$_2$- moieties may hold similar promise as the SF$_5$-phenyl molecules that have been so greatly expanded over the past few years.

Research into the SF$_5$ functional group began in the 1950s.$^{18}$ Initially, hypervalent sulfur-fluorine-containing compounds were generated by reacting thiols with high oxidation state metal fluorides, such as CoF$_3$ (Scheme 1.1).$^{19}$ These compounds were generated by electrochemical means (electrochemical fluorination, ECF) as well.$^{20}$ However, these techniques are limiting. The use of metal fluorides or electrochemical fluorination limit the number of compounds that can be generated, as these methods are generally not selective in terms of how much fluorine they put into a compound. Cost restrictions will also hamper prospective scientists from utilizing these techniques. The development of more advanced techniques and reagents designed for synthesizing pentafluorosulfanyl-containing compounds is an ongoing effort. Several reagents and techniques have been devised to allow the expansion of pentafluorosulfanyl chemistry beyond the formation of a small number of compounds.

![Scheme 1.1. Synthesis of pentafluorosulfanyl trifluoromethane by oxidative fluorination.](image-url)
The simplest compounds utilized for fluorination and pentafluorosulfanylation are compounds of the $\text{SF}_5X$ designation, where $X$ represents a fluorine, chlorine, or bromine atom. Of these compounds, $\text{SF}_6$ has the highest production, but with the least utilization as a chemical reagent.\textsuperscript{21} It is mainly used as an insulating gas for high voltage applications due to its chemical stability. The breakdown of $\text{SF}_6$ at high voltage produces toxic byproducts, such as $\text{SF}_4$. Recently, development toward the utilization of $\text{SF}_6$ as a fluorinating reagent has been made. Using a photoredox catalyst, $\text{SF}_6$ can be used as a deoxyfluorinating reagent (Scheme 1.2).\textsuperscript{22} A mechanism has been proposed for this reaction, but the proposed mechanism is based on preliminary results. Further studies of this reaction should be conducted to formally propose a mechanism. Initially, the organometallic complex transfers an electron to $\text{SF}_6$, forming a radical anion. This species is attacked by the oxygen atom of the alcohol, forming a $\text{C-O-S}_x$ species, where $x$ is equivalent to the number of fluorine atoms bonded to the sulfur atom. Currently, the number of fluorine atoms bonded to sulfur in this case is unknown. The cleavage of the C-O bond allows for the newly formed $[\text{O-S}_x]$ species to fluorinate the carbon atom. The $[\text{O-S}_x]$ species can fluorinate allylic alcohols, substituting a fluorine atom for a hydroxyl group.

Scheme 1.2. Use of $\text{SF}_6$ as a deoxyfluorinating reagent for allylic alcohols.\textsuperscript{22}
Sulfur hexafluoride can also be used to add the SF₅ group to olefins, as described in two recent journal articles (Scheme 1.3). This has been done by a photoredox method. First, N-phenylphenothiazine is excited by 365 nm light, generating a radical species. The electron from the N-phenylphenothiazine radical is transferred to SF₆, forming a SF₆ radical anion. This radical anion decomposes to a fluoride ion, as well as a pentafluorosulfanyl radical. In addition, α-phenylphenothiazine radical cation is formed. A second excitation of the N-phenylphenothiazine radical then generates a radical cation of the α-methylstyrene or α-phenylstyrene substrate. The SF₅ radical is added to the substrate, and the fluoride ion traps the product. The fluoride can be subsequently eliminated from the product, in order to generate a pentafluorosulfanyl-containing olefin. A copper salt is added to stabilize the pentafluorosulfanyl radical.

A similar radical-based technique for using SF₆ as a source of the pentafluorosulfanyl group has been reported. This technique involves the use of lithium benzophenone ketyl and 2,2,6,6-tetramethylpiperidin-1-yl (TEMPO). When the two reagents were mixed with SF₆ and an olefin, a small yield of a SF₅-containing hydrocarbon was observed. It is assumed by the authors that a single electron reduction of SF₆ occurs, producing a SF₆ radical anion, which decomposes to a SF₅ radical and lithium fluoride. The SF₅ radical then adds to the olefin, and the final product is trapped by the TEMPO radical.

Pentafluorosulfanyl chloride (SF₅Cl), as well as bromide, are two of the most ubiquitous reagents in the arena of SF₅ chemistry. The first reported synthesis of SF₅Cl involved the addition of chlorine to S₂F₁₀ (SF₅-SF₅) (Scheme 1.4).
However, this method is not widely utilized. Yields of $S_2F_{10}$ are low when the compound is not synthesized by use of $SF_5Cl$, making this route less efficient. Two alternate methods are commonly used to synthesize $SF_5Cl$. The first method involves mixing $SF_4$ with $Cl_2$ and an equimolar amount of cesium fluoride, and then heating the reaction mixture. The second method involves mixing $SF_4$ with $ClF$ and a catalytic amount of cesium fluoride. Potassium fluoride can also be used in the same way to generate $SF_5Cl$; however, this approach requires the implementation of higher temperatures and longer reaction times. A newer approach to synthesizing $SF_5Cl$ involves the use of bromine. By mixing sulfur tetrafluoride, bromine, chlorine, and cesium fluoride, $SF_5Cl$ can be generated in high yield. With this technique, the cesium fluoride can be replaced with potassium fluoride as well. However, the quantity of the potassium fluoride must be increased relative to the amount of cesium fluoride used in order to maintain the yield of $SF_5Cl$.27

Scheme 1. 3. The use of $SF_6$ as a pentafluorosulfanyl addition reagent.23
Scheme 1.4. Syntheses of sulfur chloride pentafluoride (SF₅Cl).²⁴, ²⁶, ²⁸

Pentafluorosulfanyl bromide can be formed by several different methods as well (Scheme 1.5). Mixing SF₅-SF₅ with Br₂ will generate SF₅Br.⁸, ²⁹ However, the reaction of S₂F₁₀ and bromine to form SF₅Br is reversible. By this method, the yield of SF₅Br is limited. It also can be formed by the reaction of SF₄ with BrF, in the presence of CsF. The method was improved upon by generating BrF from BrF₃ and bromine in the presence of cesium fluoride, then adding SF₄ to the mixture. Yields of SF₅Br by this method are very high, either by allowing the mixture to react at room temperature for ca. 5 weeks or with moderate heating at ca. 80 °C for 20 days. Another method developed for synthesizing SF₅Br involves mixing SF₄ and bromine in the presence of silver(I) fluoride.²⁷ By this method, yields of 75% of SF₅Br can be achieved. The reaction time can be decreased by
This method has the disadvantage of converting the silver reagent to silver bromide, requiring a second step to regenerate the silver fluoride reagent.

\[
\text{SF}_5\text{SF}_5 + \text{Br}_2 \quad \underset{138 \, ^\circ \text{C}}{\rightleftharpoons} \quad \text{SF}_5\text{Br}
\]

\[
\text{SF}_4 + \text{CsF} + \text{BrF} \quad \text{room temperature, 36 days} \quad \text{SF}_5\text{Br}
\]

\[
\text{SF}_4 + \text{AgF} + \text{Br}_2 \quad \underset{100 \, ^\circ \text{C}, 79 \, \text{h}}{\rightarrow} \quad \text{SF}_5\text{Br}
\]

Scheme 1.5. Syntheses of sulfur bromide pentafluoride (SF$_5$Br).

Both SF$_5$Cl and SF$_5$Br can be used to add SF$_5$ to alkenes and alkynes (Scheme 1.6). With mixtures of SF$_5$Cl and hydrocarbon olefins, these reactions can be initiated thermally. A variety of alkenes can be used, including cyclohexene, 1-chloroethylene, and 1-propylene among others. With cyclohexene, a by-product, thought to be 1-chloro-2-fluoro cyclohexane was also produced. When using partially or perfluorinated olefins, either photolytic initiation or free radical initiation, such as dibenzoyl peroxide, is used to carry out the reaction. In the case of hexafluoropropylene, only photolytic initiation was found to affect the addition of the pentafluorosulfanyl group to the olefin. The addition reaction has been found to be regiospecific, with the $E$-isomer being favored. The SF$_5$ group also tends to add to the carbon atom of fluoroolefins with the greater number of hydrogen atoms bonded to it. Perhaps this regiospecific addition is due to steric hindrance of the large SF$_5$ group.
With SF$_5$Br, addition reactions have been performed with several fluorinated alkenes, including tetrafluoroethylene, at room temperature (Scheme 1.7). Unlike SF$_5$Cl, SF$_5$Br will react with partially fluorinated alkenes at room temperature, due to its more reactive nature. A mechanistic study of the reaction of SF$_5$Br with cis-1,2-difluoroethylene and trans-1,2-difluoroethylene was conducted. The study indicated that SF$_5$Br reacts by a radical intermediate.$^{32}$ This is due to the amounts of erythro and threo conformers being nearly identical for reactions conducted in the dark as well as in the light. Should the reaction proceed by a bromonium intermediate, the product form should be stereospecific.

To utilize either SF$_5$Cl or SF$_5$Br as a reagent via the previously mentioned methods, either autoclaves capable of holding gases at high pressure or specialized glassware for photolytic reactions are required. This limits the ability of organic chemists to use SF$_5$Cl or SF$_5$Br. By using triethylborane as a radical initiator, SF$_5$Cl can be reacted with alkenes and alkynes at a lower temperatures and lower pressures (Scheme 1.8).$^{33}$ With this change, organic chemists could now make use of SF$_5$Cl with standard, ordinary glassware.

A similar compound, SF$_5$CF$_2$C(O)OH, can be synthesized by several different routes. It can be synthesized by adding SF$_5$Cl across the double bond in an alkyl trifluorovinyl ether and subsequent conversion to an ester followed by hydrolysis.$^{35}$

An improvement to this method was made in 2014 by Matsnev et al.$^{37}$ By synthesizing phenyl trifluorovinyl ether from a tetrafluoroethylene and carbon dioxide mixture, a trifluorovinyl ether, and subsequently SF$_5$CF$_2$C(O)OH can be made more safely in the laboratory.
Scheme 1.6. Examples of SF$_5$Cl addition reactions.$^{12,25}$

Scheme 1.7. Examples of reactions with SF$_5$Br and partially fluorinated alkenes.$^{31a,36}$
Similar to the method of Knunyants, SF$_5$Cl is added across the double bond of phenyl trifluorovinyl ether, and then the resulting intermediate is hydrolyzed in sulfuric acid to generate the acid. This carboxylic acid can also be made by adding SF$_5$Br to chlorotrifluoroethylene and hydrolyzing the addition product in oleum.$^{37}$

![Scheme 1.8. Reactions of SF$_5$Cl and alkenes catalyzed by triethylborane.$^{33}$](image)

<table>
<thead>
<tr>
<th>Product Number</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>R$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>n-C$<em>6$H$</em>{13}$</td>
<td>H</td>
</tr>
<tr>
<td>2</td>
<td>H</td>
<td>n-C$_4$H$_9$</td>
<td>H</td>
</tr>
<tr>
<td>3</td>
<td>H</td>
<td>t-C$_4$H$_9$</td>
<td>H</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>C$_2$H$_5$</td>
<td>C$_2$H$_5$</td>
</tr>
<tr>
<td>5</td>
<td>n-C$_3$H$_7$</td>
<td>n-C$_3$H$_7$</td>
<td>n-C$_3$H$_7$</td>
</tr>
<tr>
<td>6</td>
<td>(CH$_2$)$_4$</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>7</td>
<td>H</td>
<td>p-tolyl</td>
<td>H</td>
</tr>
</tbody>
</table>

From this acid, a number of products can be made ($\textbf{Scheme 1.10}$).$^{37}$ Primary and secondary amines can be mixed with SF$_5$CF$_2$C(O)OH to generate SF$_5$CF$_2$-containing amides. Additionally, esters can be prepared from SF$_5$CF$_2$C(O)OH and alkyl alcohols. From the silver salt of SF$_5$CF$_2$C(O)OH, the Borodin-Hunsdiecker reaction can be used to decarboxylate the acid and form SF$_5$CF$_2$I.$^{35}$ Additionally, heating the acid SF$_5$CF$_2$C(O)OH in the presence of phosphorus pentachloride will produce the acyl chloride, SF$_5$CF$_2$C(O)Cl.$^{37,38}$
Another important reaction which involves SF₅Cl is its addition to a nitrile group. The synthesis of SF₅N=CCl₂ was reported for the first time in 1964. This particular imine is a useful synthon with regards to SF₅N- chemistry. The SF₅N- functional group acts as a paraelement, more specifically as the oxygen atom of a carbonyl group, O=C<. In this way, SF₅N=CCl₂ should behave similarly to phosgene. This gives SF₅N=CCl₂ the likelihood of great chemical versatility, as phosgene is a commonly used reagent in the synthesis of heterocycles, amides, carbonates, and polymers. Conceivably, SF₅N=CCl₂ could be used to replace a carbonyl group with a SF₅N- functional group in almost any reaction where phosgene has been used.

Scheme 1.9. Syntheses of SF₅CH₂C(O)OH and SF₅CF₂C(O)OH.\textsuperscript{34a, 37a}
Initial experiments performed with SF₅N=CCl₂ showed that the compound can undergo substitution reactions without loss of the SF₅N- moiety. Later experiments were conducted with a number of different nucleophiles (Scheme 1.11). When SF₅NCCl₂ was mixed with an excess of sodium methoxide, SF₅N=C(OCH₃)₂ is produced. When SF₅N=CCl₂ was reacted with 2.24 equivalents of sodium phenoxide, both SF₅N=C(OC₆H₅)Cl and SF₅N=C(OC₆H₅)₂ were produced in 17% and 31% yield, respectively.

Scheme 1.10. Reactions of SF₅CF₂C(O)OH.³⁵,³⁷a

Diethylamine was also found to react with SF₅N=CCl₂ to produce SF₅N=C(Cl)N(C₂H₅), when two molar equivalents of the amine were used. This amidine
could be further substituted by reactions with phenyllithium to produce \( \text{SF}_5\text{N} = \text{C(C}_6\text{H}_5)\text{N(C}_2\text{H}_5)_2 \).

However, \( \text{SF}_5\text{NCCl}_2 \) is not the only reagent used as a crucial building block in \( \text{SF}_5\text{N} \)-chemistry. Thiazyl trifluoride is also commonly used in the synthesis of \( \text{SF}_5\text{N} \)-containing molecules.\(^{38,40}\) It can be synthesized by several different routes, but the easiest route is shown in Scheme 1.12. When mixed with two equivalents of HF, NSF\(_3\) will react to generate \( \text{SF}_5\text{NH}_2 \) (Scheme 1.11). This amine will react with acyl fluorides and chlorides to generate amides (Scheme 1.13).\(^{41}\) When NSF\(_3\) is mixed in equimolar quantities with COF\(_2\) and HF, \( \text{SF}_5\text{N(H)C(O)F} \) is formed, which will eliminate HF on contact with NaF to give \( \text{SF}_5\text{NCO} \) (Scheme 1.14).\(^{42}\)

Pentafluorosulfanyl isocyanate is also a useful reagent, as it will form urethanes when reacted with alcohols such as methanol or phenol (Scheme 1.15).\(^{42}\) This reaction can be extended to other hydrocarbon alcohols as well. The product of this reaction will have the general formula \( \text{SF}_5\text{NHC(O)OR} \), where R represents the hydrocarbon tail of the reactant alcohol. Pentafluorosulfanyl isocyanate will also react with thiols to form thioureas. When \( \text{SF}_5\text{NCO} \) reacts with primary thiols, such as methanethiol, a thiourea is formed. In the case of methanethiol, the formula of the product is \( \text{SF}_5\text{NHC(O)SCH}_3 \).

A significant development toward the synthesis of \( \text{SF}_5 \)-containing compounds was the preparation of \( \text{SF}_5 \)-containing aromatics. Pentafluorosulfanyl-substituted aromatic compounds have been more frequently used in synthesis in recent years, due to their newly found commercial availability, as well as the high stability of the pentafluorosulfanyl group when substituted into an aromatic compound. Pentafluorosulfanyl-containing aromatics were first formed in the 1960s from the oxidative fluorination of aromatic
disulfides at high temperature with silver difluoride. A slightly altered methodology employs fluorine gas mixed with nitrogen to perform a direct fluorination of aryl disulfides dissolved in acetonitrile. The most commonly used methodology employed today involves the oxidative fluorination of disulfides. Umemoto and coworkers first patented this methodology in 2009. In this method, an aryl disulfide is oxidatively fluorinated with KF and an excess of Cl₂ in acetonitrile. The resulting arylsulfur tetrafluoride chloride can be converted to an arylsulfur pentfluoride using either zinc difluoride or anhydrous hydrogen fluoride, in similar yield. The step to convert arylsulfur tetrafluoride chlorides was later improved upon by Lummer et al. By using potassium hydrogen fluoride as a source of HF, the conversion of arylsulfur tetrafluoride chlorides was improved significantly. Key to this method is the use of trifluoroacetic acid as a solvent, which can react with KHF₂ to produce HF.

A similar route to synthesize 2-pyridylsulfur pentfluorides also exists. Starting from 2,2'-dipyridyl disulfide, the compound can be oxidized by KF and chlorine in acetonitrile, and the pyridyl sulfur chlorotetrafluoride can be further oxidized by silver fluoride to form 2-pyridylsulfur pentafluoride. The reaction can be extended to form 2-pyridylsulfur pentafluorides with halogen or methyl substituents at the 3, 4, or 5 positions.

From the development of the pentafluorosulfanyl moiety, especially with regards to pentafluorosulfanyl-containing benzenes, many promising applications for the functional group are beginning to surface. However, the development of SF₅N- and SF₅CF₂-containing compounds remains largely unexplored. By increasing the availability of SF₅N- and SF₅CF₂- containing compounds, new applications may be found for these compounds. The combination of unique properties affords the SF₅ moiety a prized
position. However, the lack of availability of pentafluorosulfanyl-containing compounds, especially aliphatic SF$_5$-containing compounds, has slowed the exploration of the SF$_5$ moiety.

Scheme 1.11. Chemistry of SF$_5$NCCl$_2$.\textsuperscript{39}
By providing new synthetic routes to generate SF₅N⁻ and SF₅CF₂-containing compounds, these variations of the pentafluorosulfanyl moiety should see an increasing presence in the literature as well.

![Scheme 1. Syntheses of NSF₃ and SF₅NH₂.](image)

Scheme 1.12. Syntheses of NSF₃ and SF₅NH₂.³⁸, ⁴⁰

![Scheme 1.13. Several amidation reactions of SF₅NH₂.](image)

Scheme 1.13. Several amidation reactions of SF₅NH₂.⁴¹
The content of the following chapters will detail the original research of this dissertation. Chapter 2 contains a description of five heterocycles that have been synthesized using vicinal di-nucleophiles and SF$_5$NCCl$_2$. The synthetic techniques used to synthesize and isolate these compounds will be detailed. Additionally, the characterization of the new compounds by NMR and IR spectroscopy, as well as high-
resolution mass spectroscopy will be described. Contained within Chapter 3 is a
description of several o-pentafluorosulfanyl difluoroacetoamides synthesized by amidation
reactions of o-aminoamides and pentafluorosulfanyl difluoroacetyl chloride. In addition,
the synthesis of several quinazolin-4(3H)-ones, prepared by the cyclization of o-
pentafluorosulfanyl difluoroacetoamides in glacial acetic acid and acetic anhydride, is
discussed. The results of X-ray diffraction studies of several compounds are also
discussed. Finally, in Chapter 4, two new syntheses of SF₅CF₂H will also be discussed. A
long-awaited discussion of the NMR, IR, and Raman spectroscopy of SF₅CF₂H will also
be presented.

1.2 Thesis

Despite the unique properties of the pentafluorosulfanyl functional group, there has
been a limited exploration of the utility of the functional group. The aggressive nature of
the reagents used to add the pentafluorosulfanyl group to aliphatic compounds, and to
synthesize SF₅NCCl₂ as well as SF₅CF₂C(O)Cl have limited the ability of synthetic organic
chemists to work with the functional group. By forming SF₅-containing heterocycles from
SF₅NCCl₂ and SF₅CF₂C(O)Cl, these new heterocycles can be utilized in pharmaceutical
and materials science applications for their unique properties. Furthermore, new synthetic
methods of synthesizing SF₅CF₂H with higher yields will allow for further study of the
compound’s properties.

1.3 References

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44. Sipyagin, A. M.; Enshov, V. S.; Kashtanov, S. A.; Bateman, C. P.; Mullen, B. D.; Tan, Y.-T.; Thrasher, J. S. New 4-Pentafluorosulfanyl and 4-Perfluoroalkythio Derivatives


CHAPTER TWO
SYNTHESIS OF SF5NC< HETEROCYCLIC COMPOUNDS

2.1 Introduction

Phosgene, Cl₂C=O, is a commonly used reagent in the synthesis of five-membered heterocycles.¹ Compounds containing thiazolinone, oxazolinone, and carbonate heterocycles are some of the products derived from phosgene. These heterocycles are often known as molecular scaffolds, due to the fact that these products are subsequently developed into useful products, such as pharmaceuticals² and battery electrolytes.³ A series of modified benzothiazolonone- and benoxazolonone-containing compounds (Figure 2.1, a and b) were recently tested for their anti-inflammatory properties.⁴ Unlike other anti-inflammatory and analgesic treatments, these compounds target a different route of inflammation. The first target is inducible nitric oxide synthase, and the second target is nuclear factor kappa B. Nitric oxide synthase is responsible for the overproduction of nitric oxide in the body, leading to inflammatory conditions, such as rheumatoid arthritis. Nuclear factor kappa B signaling pathways have been indicated as contributing to the pathogenesis of chronic inflammatory diseases as well. A reduction in inflammation can be achieved by utilizing modified benzothiazolonone and benoxazolonone heterocycles.

Benzothiazolonone-containing compounds have also been recently tested as anti-cancer therapeutics. Modified benzothiazolones (Figure 2.1, c and d) can be used in conjunction with the pharmaceutical compound Olaparib to effectively kill cancer cells.⁵ This is achieved by disrupting the interaction of the BRCA2 protein with the Rad51 gene, preventing the repair of double strand breaks in DNA.²
Cyclic carbonates have a variety of applications including use as a solvent in lithium ion batteries.\textsuperscript{3} Lithium-ion batteries contain a non-aqueous electrolyte system in order to dissolve lithium salts contained within the electrochemical cell.\textsuperscript{5} Commonly, lithium-ion batteries utilize LiPF\textsubscript{6} dissolved in a mixture of cyclic and linear carbonates.\textsuperscript{6} Properties of cyclic carbonates that are desirable in batteries include high flash point, high
ionic conductivity, the ability to form a solid-electrolyte, interphase film, low melting point, and compatibility with both cathode and anode. Carbonates are also used as reactive intermediates in industrial applications. For example, five-membered alkyl carbonates, such as propylene carbonate will react with primary and secondary amines in order to generate urethanes. These urethanes can be used as a monomer feedstock for polyurethane synthesis.

The synthesis of various five-membered heterocycles using phosgene can be achieved starting from a variety of 1,2-binucleophiles. The carbon atom of phosgene can be attacked by nucleophiles. A substitution of the nucleophile for a chlorine atom occurs, producing a new carbon to nucleophile bond and one molar equivalent of HCl. This reaction can occur either once or twice at the carbon atom in phosgene. By controlling the stoichiometry of the reaction, either monosubstituted or disubstituted products can be generated, as well as larger polymeric chains, or heterocycles. A one-to-one molar equivalent ratio of phosgene to nucleophile will result in a product that has only one of the chlorine atoms of phosgene being substituted by the nucleophile. A ratio of two molar equivalents of a nucleophile to one molar equivalent of phosgene will result in a disubstituted product. In order to form heterocyclic compounds, phosgene can be mixed with organic compounds that have two or more nucleophilic groups bonded to the compound. A base, such as sodium hydroxide, triethylamine, or pyridine is used to accelerate the reaction. By mixing phosgene with 1,2-, 1,3-, and 1,4-glycols, cyclic carbonates consisting of 5-, 6-, or 7-membered rings can be constructed. Diamines, such as ethylene diamine can also be used to form heterocycles with phosgene. Similar reaction conditions are also employed. Polymers can also be produced from reactions of phosgene and organic compounds with multiple nucleophilic groups. To form polymers instead of heterocycles, the reaction conditions are altered. When forming polymers, the
concentration of phosgene in solution is significantly increased, as well as the reaction temperature. Certain diamines and glycols are not capable of forming heterocyclic structures but can be used to form polymers. For example, aromatic diamines or diphenol compounds where the nucleophilic groups are positioned para to each other will yield polymeric compounds rather than heterocycles.

The concept of isosterism was first discussed by Irving Langmuir in 1919. It was focused on the configuration of electrons around the nuclei of atoms. This concept is used to help explain the similarity of molecules that have the same number and configuration of electrons, but differing nuclei comprising their respective structures. Langmuir describes the concept with, “Comolecules are thus isosteric if they contain the same number and arrangement of electrons.”

The concept was further expanded upon by Grimm which later became known as Grimm’s hydride displacement law. The law states, “Atoms anywhere up to four places in the periodic system before an inert gas change their properties by uniting with one to four hydrogen atoms, in such a manner that the resulting combinations behave like pseudoatoms, which are like elements in the groups one to four places, respectively, to their right.” In practice, this principle means that by adding a hydrogen atom to an element, its properties will resemble that of the atom that has one higher atomic number. An example of this would be the -CH ligand, which is isosteric with the nitrogen atom. Extending this concept further, a -CH₃ ligand is isosteric with the fluorine atom.

Grimm’s hydride displacement law has been used as a basis to help explain the behavior of the fluorine atom and its properties. Fluorine can form monovalent bonds with other elements, similarly to hydrogen. The van der Waals radii of the two elements
are comparable, with the radius of a hydrogen atom being 1.2 Å, while the radius of a fluorine atom is 1.35 Å. However, unlike hydrogen, elements that form bonds with fluorine will not be isoelectronic with the elements to the right in the periodic table. To distinguish between the ligands generated by hydrogen, and those with fluorine, the term “paraelement,” has been devised for the ligands formed with fluorine. Paraelements should act similarly to pseudoelements in terms of their ligand properties. For example, a CF₃ ligand is a paraelement of fluorine, just as -CH₃ is a pseudoelement of fluorine. However, these paraelements often impart wildly different properties to the compounds in which they are found. A famous example of a fluorine substitution is that of 5-fluorouracil. With the substitution of a single fluorine atom, uracil is transformed from a component of RNA to an anti-neoplastic agent. However, the two compounds are isovalent with each other, and the fluorine atom of 5-fluorouracil can be considered as a paraelement.

The paraelement concept has been extended to the pentafluorosulfanyl moiety. With five fluorine atoms bonded to sulfur, the compound is one electron short of having a totally filled valence shell, and it can be considered a paraelement of a halogen atom. Each paraelement formed can act as a subsequent ligand to form a new paraelement. When the SF₅ group is bonded to nitrogen, a first order paraelement of oxygen is formed.

By forming a compound that has a double bond between a carbon atom and the nitrogen atom bonded to an SF₅ group, a second order paraelement can be formed that would mimic the carbonyl group. Due to the ubiquity of the carbonyl functionality throughout organic chemistry, a vast number of compounds exists where the SF₅N= group can be substituted for the oxygen atom in a carbonyl functionality. This replacement may provide the SF₅N=C<-containing compound with advantageous properties.
The largest issue with replacing the oxygen atom of a carbonyl functional group with the SF$_5$N= group is finding a synthetic method to achieve this goal. Discussed earlier, SF$_5$N=CCl$_2$ should act as an analogue of phosgene. Due to the widespread use of phosgene as a reagent for the synthesis of industrial compounds, SF$_5$N=CCl$_2$ may have the potential to be used as a building block for many compounds that contain the SF$_5$N=C< functional group. Through earlier experiments, SF$_5$N=CCl$_2$ has been shown have similar reactivity to phosgene.$^{18}$ The first synthesis of SF$_5$NCCl$_2$ appeared in 1964 when a mixture of SF$_5$Cl and ClCN was photolyzed as shown in Scheme 2.1.$^{19}$

![Scheme 2.1. The synthesis of SF$_5$NCCl$_2$.](image)

The first report of a SF$_5$NC<-containing five-membered heterocycle appeared in 1993, and that heterocycle was further oxidized to the mono- and the dinitro derivatives as shown in Scheme 2.2.$^{20}$ To synthesize the five-membered heterocycle, SF$_5$NCCl$_2$ was mixed with ethylene diamine in order to generate a para-2-imidazolidonone ring. The structure described in this literature could be reacted with various substances, and nitration of the ring proved to be possible, without decomposition of the SF$_5$NC< functional group.
Herein, new SF₅NC- containing compounds synthesized in the laboratory of Dr. Thrasher are reported. The compound SF₅NCCl₂ was reacted with oxygen, nitrogen, and/or sulfur nucleophiles, to form cyclized products. Two types of bases were also used in these attempts, including sodium salts of the nucleophiles, as well as pyridine.

Scheme 2.2. The synthesis of the first SF5NC- containing five-membered heterocycle.²⁰

Pyridine was used in the synthesis of compound 4, while sodium salts of the 1,2-binucleophiles were formed *in situ* prior to the addition of SF₅NCCl₂ in the preparation of compounds 1, 2, 3, and 5 (*vide infra*).
2.2 Experimental

2.2.1 Reagents and synthetic equipment

Ortho-aminothiophenol was purchased from Acros Organics, while catechol was purchased from Tokyo Chemical Industry Co. Pinacol and o-aminophenol were purchased from Alfa Aesar, while ethylene glycol, sodium hydride, and pyridine were purchased from Sigma-Aldrich. Argon was purchased from Airgas. Pinacol and o-aminophenol were recrystallized from 1-propanol and water and subsequently dried in a vacuum oven before use. All other reagents were used as received. All reactions were carried out in either 316-stainless steel Hoke® cylinders or in Pyrex glassware.

All $^{19}$F NMR (283 MHz), $^1$H NMR (300 MHz), and $^{13}$C NMR (75.5 MHz) spectra were recorded on a JEOL ECX-300 NMR spectrometer. The abbreviations used to describe signal multiplicity in the NMR spectra are as follows: s-singlet, bs-broad singlet, d-doublet, t-triplet, q-quartet, qn-quintet, and m-multiplet. Chemical shifts (δ) are presented in ppm downfield from CDCl$_3$ or CD$_3$C(O)CD$_3$ for $^1$H NMR and $^{13}$C NMR spectroscopy, and from CCl$_3$F for $^{19}$F NMR spectroscopy. The ATR-FT-IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer with an iD5 ATR-IR accessory, with a resolution of 4 cm$^{-1}$. High-resolution mass spectrometry analyses were carried out at The University of Alabama (Tuscaloosa, AL). Single crystal X-ray data was collected on a Bruker D8 Venture instrument. The structures were solved and refined by using full-matrix least-squares on F$^2$ method with Bruker SHELXTL software.

2.2.2 Synthesis of sulfur chloride pentafluoride ($SF_5Cl$)$^{21}$

To a 500-mL 316-stainless steel Hoke cylinder, 15 g of powdered, anhydrous cesium fluoride was added in a dry box. The cylinder was capped with a 316-stainless steel Swagelok valve in the dry box, and then the cylinder was evacuated using a vacuum line. Next, 54 g (0.50 mol) of sulfur tetrafluoride and 27 g (0.5 mol) of chlorine monofluoride
were condensed to the cylinder. This addition was performed in a stepwise manner. An aliquot of 0.1 mol of sulfur tetrafluoride and 0.1 mol of chlorine monofluoride were both condensed to the cylinder. After the compounds were condensed to the cylinder, the cylinder was sealed, disconnected from the vacuum line, and allowed to slowly warm to room temperature behind a blast shield. Once the cylinder had warmed to room temperature, it was subsequently re-connected to the vacuum line to add another aliquot of sulfur tetrafluoride and chlorine monofluoride. This process was repeated until 0.5 mol of sulfur tetrafluoride and 0.5 mol of chlorine monofluoride were added to the cylinder. The cylinder was allowed to warm to room temperature and was shaken for 5 days. After this, the contents of the cylinder were separated using trap-to-trap distillation. Three traps were used. The two traps closest to the cylinder were held at -126 °C, while the last trap was held at -196 °C. The product mainly collected in the first trap held at -126 °C. The purity of the collected product was checked by FT-IR spectroscopy, then transferred to an empty 316-stainless steel Hoke cylinder for storage. One of the possible impurities in the sample, chlorine, cannot be observed using FT-IR spectroscopy. The materials that passed to the third trap were returned to the reaction cylinder for further reaction.

An alternative procedure for adding the gases can be used. By this method, 0.5 mol of sulfur tetrafluoride and 0.1 mol of chlorine monofluoride are condensed to the cylinder, then the cylinder is warmed slowly to room temperature behind a blast shield. Over the course of the next four days, 0.1 mol of chlorine monofluoride is added to the cylinder, until 0.5 mol of chlorine monofluoride is added to the cylinder. Upon the final addition of chlorine monofluoride, the cylinder shaken at room temperature for 24 hours before the contents of the cylinder are distilled.
2.2.3 Synthesis of pentafluorosulfanyldichloroimine (SF\textsubscript{5}NCCl\textsubscript{2})\textsuperscript{19}

To begin, a 22-L round-bottomed flask equipped with a Kontes\textregistered stopcock valve joint, as well as a quartz well in the center, was evacuated for a 24-hour period on a vacuum line. Next, 65 g (0.40 mol) of sulfur chloride pentafluoride and 25 g (0.4 mol) of cyanogen chloride were condensed into the flask by vacuum transfer. The flask was moved to a fume hood and masked with aluminum foil. The hood sash was also masked with aluminum foil. Afterward, a 15-W mercury vapor lamp, such as the Ace Glass 12132-08 UV lamp, was gently lowered into the quartz well of the flask and turned on. The contents of the flask were irradiated for 5 days. After the irradiation had ceased, the contents of the flask were transferred on a vacuum line to an empty 300-mL, 316-stainless steel Hoke cylinder topped with a 316-stainless steel Swagelok valve. The contents of the cylinder were separated by trap-to-trap distillation. Two traps were used to separate the product. The trap closest to the cylinder was held at -70 °C, while the second trap was held at -196 °C. The product was collected in the first trap, while unreacted starting materials were collected in the second trap. The purity of the product was checked by IR and \textsuperscript{19}F NMR spectroscopy. The unreacted starting materials were returned to the 22-L flask for further reaction, while the product was transferred to a sealable glass container. \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 283 MHz) δ 64.8 ppm (d, \textsuperscript{2}J\textsubscript{F-F} = 161 Hz, 4 F), 71.8 (qn, 1 F). FT-IR 1676, 1641, 1623, 916, 734, 678, 640 cm\textsuperscript{-1}.\textsuperscript{22}

2.2.4 Synthesis of N-pentafluorosulfanyl-1,3-benzothiazol-2-imine (Compound 1)

To a two-necked, 250-mL round-bottomed flask, equipped with a Kontes\textregistered valve adaptor, a PTFE-coated magnetic stir bar, and a septum, 0.096 g (4.0 mmol) of sodium hydride was added in a dry box. Next, 10 mL of anhydrous tetrahydrofuran was added by syringe. At this point, a Krytox®-containing oil bubbler was connected to the flask. The reaction flask was then chilled to 0 °C. Slowly, 0.50 g (4.0 mmol) of anhydrous o-
aminothiophenol was dripped into the flask. Concurrently, the solution in the flask was stirred using the magnetic stir bar. After the o-aminothiophenol had been added, the flask was warmed to ambient temperature and stirred for several hours. The flask was then connected to a vacuum line, chilled to liquid nitrogen temperature, and 0.90 g (4.0 mmol) of pentafluorosulfanyldichloroimine was condensed into the flask. The flask was then warmed to -78 °C, and the reaction mixture stirred for 2 hours. After this, the reaction mixture was warmed to room temperature and stirred overnight. The THF was then removed by a rotary evaporator, and the reaction products extracted with dichloromethane and water. The organic layer was evaporated, and the product recrystallized from a mixture of 90% dichloromethane and 10% acetone. The yield is 0.36 g, 33%. In an attempt to find the melting point of compound 1, it was found to decompose at 128-130 °C. \(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta 7.20 (t, 1\text{H}), 7.31 (m, 2\text{H}), 7.70 (d, 1\text{H}), 11.44 (s, 1\text{H})\). \(^{19}\)F NMR (CDCl\(_3\), 283 MHz) \(\delta 68.9 (d, ^2J_{\text{F-F}} = 155 \text{ Hz}, 4 \text{ F}), 93.4 (\text{qn}, 1 \text{ F})\). \(^{13}\)C NMR (CDCl\(_3\), 75.5 MHz) \(\delta 112.7, 122.2, 123.6, 127.5, 127.5, 137.0, 165.1 (\text{qn}, ^2J_{\text{C-F}} = 3.78 \text{ Hz})\). ATR-IR (film) 3189 (w), 1603 (w), 1560 (m), 1468 (m), 1408 (w), 1315 (w), 1295 (w), 1256 (w), 1160 (w), 1076 (w), 1025 (w), 940 (m), 811 (vs), 739 (vs), 665 (s), 630 (m), 577 (s), 564 (m) cm\(^{-1}\). HRMS (EI) mass calculated for (C\(_7\)H\(_5\)N\(_2\)F\(_5\)S\(_2\)) calcd.: 275.9814, found: 275.9813.

### 2.2.5 Synthesis of N-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2)

To a one-necked 25-mL round-bottomed flask equipped with a PTFE-coated magnetic stir bar and a septum, 0.10 g (4.0 mmol) of sodium hydride was added in a dry box. To a second one-necked 25-mL round-bottomed flask equipped with a septum 0.22 g (2.0 mmol) of catechol was added in a dry box. Both flasks were removed from the dry box, and 5 mL of anhydrous THF was added to each flask. The flask containing sodium hydride was placed in an ice bath, situated on top of a stir plate, and an oil bubbler was
connected to the flask. The sodium hydride slurry was stirred, and the catechol solution was slowly dripped in. After the catechol solution had been dripped into the flask, the resulting solution was slowly warmed to ambient temperature and allowed to stir for several hours. Next, 5 mL of a 0.4 M SF₅NCCl₂ solution in THF was prepared. The flask containing sodium hydride and catechol was chilled to -78 °C, and the SF₅NCCl₂ solution was slowly dripped in. After the SF₅NCCl₂ solution had been dripped in, the flask was slowly warmed to ambient temperature, and its contents were stirred for 14 days. ¹⁹F NMR spectroscopy was used to ensure the completion of the reaction. The reaction mixture was diluted with THF, and the solid components were removed by filtration. The filtrate was evaporated by rotary evaporation, and the solid contents were purified by sublimation. Using a vacuum sublimator held at a pressure of 0.001 mmHg, the product was collected on a cold finger held at 0 °C. The yield is 0.29 g, 56%. A melting point was not found for compound 2. ¹H NMR (CDCl₃, 300 MHz) δ 7.43-7.46 (m, 2 H), 7.59-7.62 (m, 2 H). ¹⁹F NMR (CDCl₃, 283 MHz) δ 73.4 (d, ²J_F,F = 161 Hz, 4F), 82.7 (qn, 1 F). ¹³C NMR (CDCl₃, 75.5 MHz) δ 110.9 (s), 115.5 (s), 121.2 (s), 125.8 (m), 154.9 (qn, ²J_C,F = 6.8 Hz). ATR-IR (film) 1698 (m), 1637 (m), 1538 (w), 1514 (w), 1475 (m), 1444 (w), 1356 (w), 1334 (w), 1298 (w), 1274 (m), 1237 (m), 1157 (w), 1130 (w), 1051 (w), 1002 (w), 936 (w), 893 (w), 857 (s), 840 (s), 793 (s), 756 (w), 742 (s), 718 (s), 667 (s), 588 (s), 577 (s) cm⁻¹. HRMS (El) mass calculated for (C₇H₄NO₂F₅S) calcd.: 260.9883, found: 260.9881.

2.2.6 Synthesis of N-pentafluorosulfanyl-1,3-benzoazol-2-imine (Compound 3)

To a 25-mL round-bottomed flask equipped with a stir bar, 0.15 g (6.3 mmol) of NaH was added in a dry box. Next, 10 mL of an anhydrous 0.32 M solution of o-aminophenol in THF was formed. The flask containing the sodium hydride was placed in an ice bath and connected to an oil bubbler. The THF solution was slowly dripped into the flask containing the sodium hydride over 30 minutes. Once the dripping was complete, the
flask was warmed to room temperature, and its contents were stirred for several hours. Then, 0.72 g (3.2 mmol) of SF$_5$NCCl$_2$ was condensed into a flask. The SF$_5$NCCl$_2$ was diluted with 5 mL of anhydrous THF. The flask containing the sodium hydride and o-aminophenol was then chilled to -78 °C, an argon balloon was connected to the flask, and the SF$_5$NCCl$_2$ solution was slowly dripped in. Once the SF$_5$NCCl$_2$ was completely added, the flask was warmed to room temperature, and allowed to stir for 17 days. At this point, the THF was removed by rotary evaporation, and the reaction products were extracted by a mixture of ethyl acetate and water. The organic layer was dried on MgSO$_4$, filtered and evaporated. The products were then recrystallized several times from a mixture of hexanes and ethyl acetate (90:10). The isolated product was dissolved in a solution of hexanes and acetone (50:50), and the solvent was slowly evaporated. The crystals recovered from this process were suitable for X-ray diffraction. The yield is 0.19 g, 23%.

The compound was found to decompose at 180 °C when an attempt was made to find the melting point. $^1$H NMR (acetone-$d_6$, 300 MHz) $\delta$ 7.23-7.32 (m, 3 H), 7.46 (d, 1 H), 11.3 (bs, 1H). $^{19}$F NMR (acetone-$d_6$, 283 MHz) $\delta$ 74.5 (d, $^{2}$J$_{F,F}$ = 156 Hz, 4 F), 92.9 (qn, 1 F). $^{13}$C NMR (acetone-$d_6$, 75.5 MHz) $\delta$ 110.4 (s), 111.1 (s), 123.6 (s), 125.3 (s), 129.8 (m), 144.9 (s). ATR-IR (film) 2801 (w), 2360 (w), 2339 (w), 1662 (s), 1632 (m), 1477 (s), 1361 (m), 1259 (w), 1041 (m), 1004 (w), 912 (w), 864 (s), 839 (s), 803 (s), 745 (s), 729 (s), 668 (s), 623 (w), 585 (s), 577 (s), 548 (m) cm$^{-1}$.

2.2.7 Synthesis of 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4)

To a 100-mL round-bottomed flask equipped with a magnetic stir bar, 0.30 g (2.5 mmol) of anhydrous pinacol was added. This step was carried out in a dry box. The flask was topped with a septum and placed on a magnetic stir plate within a fume hood. Next, 50 mL of anhydrous THF was added to the flask via syringe. After the addition of
THF, 0.40 mL (5.0 mmol) of anhydrous pyridine was added to the flask. An argon filled latex balloon was connected to the flask via syringe. During this period, the flask was cooled to -78 °C. Once the flask had been chilled for 15 minutes, 5 mL of a 0.5 M solution consisting of SF₅NCCl₂ in anhydrous THF was slowly dripped into the flask over the period of 45 minutes. Once the solution had been added, the flask was held at -78 °C for two hours, and then it was allowed to warm slowly to ambient temperature. The reaction contents were stirred at room temperature for 11 days. Thereafter, the contents of the reaction mixture were filtered, and the THF was removed by rotary evaporation. The remaining solid was isolated by vacuum sublimation. The yield is 0.37 g, 55%. The melting point is 126-128 °C. The recovered product was dissolved in acetone, and the solvent was slowly evaporated in order to grow suitable crystals for X-ray diffraction studies. ¹H NMR (acetone-d₆, 300 MHz) δ 1.39 (bs, 9 H), 1.50 (bs, 3 H). ¹⁹F NMR (acetone-d₆, 283 MHz) δ 73.9 (d, 2J_F-F = 153 Hz, 4 F), 88.8 (qn, 1 F). ATR-IR (film) 2988 (w), 1770 (m), 1652 (w), 1489 (w), 1456 (w), 1388 (w), 1377 (m), 1283 (w), 1221 (w), 1177 (m), 1149 (m), 1089 (m), 1063 (w), 1031 (m), 1009 (m), 962 (w), 882 (w), 869 (w), 841 (w), 783 (s), 748 (m), 716 (m), 671 (m), 629 (m), 600 (m), 583 (m) cm⁻¹.

2.2.8 Synthesis of N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5)

To a 100-mL three-necked round-bottomed flask equipped with a magnetic stir bar, 0.048 g (4.0 mmol) of sodium hydride were added in a dry box. The flask was removed from the dry box and placed on a stir plate. Next, the flask was filled with 10 mL of anhydrous THF via syringe. The flask was connected to a Krytox® oil bubbler and placed in an ice bath. Slowly, 0.12 g (2.0 mmol) of ethylene glycol was dripped into the flask over 30 minutes. The ice was removed, and the mixture was stirred for several hours. The flask was then connected to a vacuum line, cooled to liquid nitrogen temperature, and 0.45 g (2.0 mmol) of pentafluorosulfanyldichloroimine was condensed into the flask. The flask
was then placed in a -78 °C bath on a magnetic stir plate, and its contents were then allowed to warm to room temperature. After warming to room temperature, the mixture was stirred for an additional 1 hour. Afterward, the mixture was filtered, and the solvent was evaporated. Several small crystals were recovered after the evaporation of the solvent, which were of suitable quality for X-ray diffraction studies. The yield is 0.008 g, 2%. The melting point is 70 °C. $^{19}$F NMR (acetone-$d_6$, 283 MHz) δ 73.3 (d, $^2J_{F-F} = 156$ Hz, 4 F); 85.4 (qn, 1 F). ATR-IR (film) 1803 (w), 1661 (m), 1481 (m), 1419 (m), 1229 (s), 1210 (m), 1121 (s), 1075 (w), 994 (w), 917 (m), 815 (s), 731 (s), 651 (s), 590 (s), 571 (s) cm$^{-1}$. HRMS (El) mass calculated for (C$_7$H$_4$NO$_2$F$_5$S) calcd.: 212.9883, found: 212.9889.

2.2.9 Attempted preparation of (Z)-3-butyl-N-(pentafluorosulfanyl)benzo[d]thiazol-2(3H)-imine

To a 10 mL, round-bottomed flask, equipped with a stir bar, 0.10 g (0.36 mmol) of compound (1) was added. Next, the flask was sealed with a septum. At this time, 5 mL of anhydrous THF was added to the flask. Now, 0.050 g (0.36 mmol) of 1-bromobutane is added to the flask. The flask was chilled to 0 °C, and 0.056 g (0.36 mmol) of 1,8-diazabicyclo[5.4.0]undec-7-ene was added to the flask. The reaction solution turned a reddish color several minutes after the addition of DBU. The reaction solution was allowed to warm to room temperature slowly and was stirred for several days. Afterwards, the THF was removed via rotovap, leaving behind a brown oil. All attempts to recover the reaction products failed.
2.2.10 Attempted preparation of 2-hydroxyphenyl \( N' \)-pentafluorosulfanyl-\( N \)-dodecylcarbamimidate

To a 10 mL, round-bottomed flask, equipped with a stir bar, 0.10 g (0.38 mmol) of compound (2) was added in a dry box, then capped with a septum. The flask was removed from the dry box, and 5 mL of anhydrous THF was injected into the flask. Now, 0.071 g (0.38 mmol) of 1-dodecylamine was injected into the flask. The reaction solution turned to a dark red color over the course of one hour. After 24 hours, the THF was removed from the reaction solution via rotovap. A dark red colored oil remained in the flask. All attempts to isolate the reaction products from the reaction mixture failed.

2.3 Results and Discussion

Using pentafluorosulfanyldichloroimine as a substitute for phosgene, new heterocyclic products can be synthesized as shown in Scheme 2.3. When forming compounds 2-5, two equivalents of sodium hydride were added to the corresponding 1,2-binucleophiles in anhydrous THF, in order to form the disodium salts of the binucleophiles. In the case of compound 1, only one equivalent of sodium hydride was used to form a sodium salt with the 1,2-binucleophile. It is not known whether a smaller quantity of disodium salt was formed, or if the monosodium salt will successfully form the corresponding heterocycle. These salts were then reacted with pentafluorosulfanyldichloroimine to form five-membered heterocycles. Several different classes of \( \text{SF}_5 \)-substituted heterocycles can be formed, including 1,3-benzothiazol-2-imines, 1,3-benzodioxol-2-imines, and 1,3-benzoxazol-2-imines. These new heterocycles were characterized with NMR spectroscopy, single crystal X-ray diffraction, and high-resolution mass spectroscopy (HRMS).
Previously reported SF$_5$N=C< containing compound N-pentafluoro-sulfanyl-imidazolidin-2-imine, shown in Scheme 2.2, as well as the five-membered heterocycles illustrated in Figure 2.2: 1,3-benzothiazol-2(3H)-one, 1,3-benzoaxazol-2(3H)-one, 1,3-benzodioxol-2-one, 1,3-dioxolan-2-one, and 4,4,5,5-tetramethyl-1,3-dioxolan-2-one were used as a point of comparison for the NMR, FT-IR, and mass spectral analyses. The SF$_5$N=C< containing compounds were used to compare the $^{19}$F NMR spectra of the newly synthesized compounds. With regards to $^1$H NMR and $^{13}$C NMR spectra, comparisons were made between the spectra of compounds 1-5 to 1,3-benzothiazol-2(3H)-one, 1,3-benzodioxol-2-one, 1,3-benzoaxazol-2(3H)-one, 4,4,5,5-tetramethyl-1,3-dioxolan-2-one, and 1,3-dioxolan-2-one, respectively. The previously synthesized compounds used for the $^1$H NMR spectral analysis and $^{13}$C NMR spectral analysis feature a carbonyl moiety in the same position where the SF$_5$N- functional group would be for compounds 1-5. This point of comparison is the only difference in the constitution of the reference compounds and compounds 1-5. Due to this factor, the effect that the SF$_5$N- functional group has on the $^1$H NMR and $^{13}$C NMR spectra of the compounds can be observed. As shown in Scheme 2.3, the synthesis of five-membered heterocycles 1-5, containing the SF$_5$N=C< moiety involved the use of SF$_5$NCCl$_2$ reacting with a 1,2 binucleophile, and a base, either sodium hydride or pyridine.$^{18,20}$

The examples of heterocycles presented herein show a greater diversity in the heteroatoms that make up the cyclic structures. Examples of carbonate-like structures, as well as a thiazolone-like structure and an oxazole-like structure have been synthesized. All five compounds take the form of colorless, crystalline solids during recrystallization. By expanding upon the variety of heteroatoms used, the synthetic utility of SF$_5$NCCl$_2$ has been expanded.
As expected, the $^{19}$F NMR spectra shown in the Appendix (Figure A.1, Figure A.7, Figure A.13, Figure A.19, and Figure A.22) of all five compounds (1-5) display characteristic AB$_2$ patterns of SF$_5$ fluorine atoms, and the signals of the A fluorine atoms appear upfield from those of the equatorial fluorine atoms. The range in chemical shifts for the B portion of each spectra is 4.4 ppm, while the range in chemical shifts for the A portion of each spectra is 10.7 ppm.

Scheme 2.3. Syntheses of SF$_5$NC$<$ containing five-membered heterocycles.
Figure 2.2. Compounds used for $^1$H NMR chemical shift comparison.

The variation in the signals’ chemical shifts is likely due to differing chemical environments because of the various heteroatoms which comprise each heterocycle. The different solvents used for measurements may also play a role in the variation. The chemical shifts and coupling constant are listed in Table 2.1, which fall in the reported range.

The $^1$H NMR spectra of compounds 1-4 are shown in the Appendix (Figure A.1, Figure A.6, Figure A.12, and Figure A.18). The aromatic protons of compound 1-3 exhibit chemical shifts between 7.20-7.62 ppm, while the N-H protons are typically located at approximately 10 ppm as listed in Table 2.2. These spectra can be compared to those of compounds with equivalent ring structures, save for the substitution of the SF$_3$N- moiety for a carbonyl moiety.
Table 2.1. Chemical shifts and coupling constants of SF₅ fluorine atoms in ¹⁹F NMR spectra.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Axial F Chemical shift (ppm)</th>
<th>Coupling constant (Hz)</th>
<th>Equatorial F chemical shift (ppm)</th>
<th>Coupling constant (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>93.4</td>
<td>158.5</td>
<td>68.9</td>
<td>155.7</td>
</tr>
<tr>
<td>2</td>
<td>82.7</td>
<td>155.7</td>
<td>73.4</td>
<td>158.5</td>
</tr>
<tr>
<td>3</td>
<td>92.9</td>
<td>158.5</td>
<td>74.6</td>
<td>155.7</td>
</tr>
<tr>
<td>4</td>
<td>88.8</td>
<td>158.5</td>
<td>73.9</td>
<td>152.8</td>
</tr>
<tr>
<td>5</td>
<td>85.4</td>
<td>152.8</td>
<td>73.4</td>
<td>155.7</td>
</tr>
</tbody>
</table>

The presence of a SF₅N- functional group would change the symmetry of the molecules relative to the carbonyl group, which presents more complexity in both ¹H NMR and IR spectra. A common feature of all five compounds is the presence of a C=N imino bond. These peaks are most likely correlated with this imino bond. A second similarity between compounds 1-5 is the pentafluorosulfanyl functional group. A set of two peaks between 800 and 950 cm⁻¹ are correlated to this functional group. Deformations arising from the sulfur to fluorine bonds in compounds 1-5 are also observed from 577 to 600 cm⁻¹. These two absorptions can be seen in all five compounds. Compounds 1, 2, and 3 feature a phenylene ring fused to the five-membered heterocycle of each compound. Due to this, an IR absorption is observed at 3189 cm⁻¹ for compound 1, and 2801 cm⁻¹ for compound 3. These spectra can be compared to those of compounds with equivalent ring structures, save for the substitution of the SF₅N=C moiety for a carbonyl moiety. The presence of a SF₅N- functional group would change the symmetry of the molecules relative to the carbonyl, which causes more complexity in both ¹H NMR and IR spectra.
Table 2.1. $^1$H NMR chemical shifts of compound 1-5 and their reference compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Aromatic H chemical shift (ppm)</th>
<th>NH proton chemical shift (ppm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-benzothiazoleone</td>
<td>7.39-7.41 (m), 7.26-7.30 (m), 7.16-7.19 (m), 7.14 (s)</td>
<td>10.4</td>
<td>21</td>
</tr>
<tr>
<td>Phenylene carbonate</td>
<td>7.43-7.46 (m), 7.59-7.62 (m)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3,3-benzoxazol-2(3H)-one</td>
<td>7.47-6.91 (m)</td>
<td>8.18</td>
<td>20(f)</td>
</tr>
<tr>
<td>4,4,5,5-tetramethyl-1,3-dioxolan-2-one</td>
<td>1.40 (s)</td>
<td>N/A</td>
<td>20(a)</td>
</tr>
</tbody>
</table>

As listed in Table 2.3, the IR spectra of compounds 1-5 share several similarities, despite the structural difference of each compound. In the spectrum of each compound, a peak of medium intensity can be observed between 1600 cm$^{-1}$ and 1670 cm$^{-1}$. A common feature of all five compounds is the presence of a C=N imino bond. These peaks are most likely correlated with this imino bond. A second similarity between compounds 1-5 is the pentafluorosulfanyl functional group. A set of two peaks between 800 and 950 cm$^{-1}$ are correlated to this functional group. Deformations arising from the sulfur to fluorine bonds in compounds 1-5 are also observed from 577 to 600 cm$^{-1}$. These
two absorptions can be seen in all five compounds. Compounds 1, 2, and 3 feature a phenylene ring fused to the five-membered heterocycle of each compound. Due to this, an IR absorption is observed at 3189 cm\(^{-1}\) for compound 1, and 2801 cm\(^{-1}\) for compound 3. Despite the presence of a phenylene group in compound 2, no IR absorption is seen at around 3000 cm\(^{-1}\). Compound 4 features four methyl groups as part of its structure. These groups are related to the absorption observed at 2988 cm\(^{-1}\).

Table 2.3. C=\(\text{N}\) and S-F IR vibrational bands of compounds 1-5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C=(\text{N}) (cm(^{-1}))</th>
<th>S-F (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1603</td>
<td>940, 811, 577</td>
</tr>
<tr>
<td>2</td>
<td>1637</td>
<td>857, 840, 588</td>
</tr>
<tr>
<td>3</td>
<td>1632</td>
<td>864, 839, 585</td>
</tr>
<tr>
<td>4</td>
<td>1652</td>
<td>869, 841, 600</td>
</tr>
<tr>
<td>5</td>
<td>1661</td>
<td>917, 815, 590</td>
</tr>
</tbody>
</table>

The crystal structures of all five compounds are shown in Figure 2.3. Heterocycles compound 1-3 contain the aromatic rings fused with a five-membered ring, which exhibit a planar structure excluding the SF\(_{5}\) group. Compound 4 and 5 are lacking aromatic rings in their structures. Therefore, the five-membered heterocycles of compound 4 and 5 exhibit bent conformations and lower symmetries. Atoms O1-O2-C3-C2 of compound 4 do not lie within one plane; neither do the atoms O1-O2-C2-C3 of compound 5. The SF\(_{5}\) groups of compounds 1 and 3 deflect towards the S2 atom and O1 atom, respectively, which perhaps is caused by the steric effect of the hydrogen atom attached to N2 atoms in each structure. Whether the hydrogen atom is attached to N1 atom or N2 atom in
compound 1 and 3 is determined by measuring the bond length of C1-N1 and C1-N2 in both structures. As listed in Table 2.4, the sp²-hybridized C-N bonds in compounds 2, 4, and 5 are approximately 1.28 Å, while the C-N bonds in compounds 1 and 3 are longer than 1.28 Å. The C1-N2 bond distance in compound 1 and the C1-N2 bond distance in compound 3 are approximately 1.35 Å, which are significantly longer than 1.28 Å, and it indicates that these two C1-N2 bonds are single bonds, thus the hydrogen atom is likely to be attached to the N2 atom in both compounds 1 and 3.

Figure 2.3. Crystal structures of compounds 1-5. Color code: Green-fluorine, blue-nitrogen, yellow-sulfur, red-oxygen, grey-carbon, and white-hydrogen.

For all five compounds, the S-F bond lengths range from approximately 1.57 to 1.60 Å. The longest S-F bonds correspond to the axial sulfur fluorine bond in each case. In the case of the shortest sulfur to fluorine bond, it is directed away from the heteroatom
close to the sulfur atom of the pentafluorosulfanyl group. This is true of compounds 1, 2, 3, and 5, and partially true for compound 4. As compound 4 has two smallest sulfur to fluorine bonds of equal length, one of the small equatorial sulfur to fluorine bonds of this compound is not directed away from the heteroatom closest to the pentafluorosulfanyl sulfur atom. The bond angles between the equatorial fluorine atoms, the sulfur atom, and the axial fluorine atom of each compound are slightly smaller than 90°.

Table 2.4. C-N bond lengths in compounds 1-5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C1-N1</td>
<td>1.318(6)</td>
</tr>
<tr>
<td></td>
<td>C1-N2</td>
<td>1.344(6)</td>
</tr>
<tr>
<td>2</td>
<td>C1-N1</td>
<td>1.2772(14)</td>
</tr>
<tr>
<td>3</td>
<td>C1-N1</td>
<td>1.303(4)</td>
</tr>
<tr>
<td></td>
<td>C1-N2</td>
<td>1.345(4)</td>
</tr>
<tr>
<td>4</td>
<td>C1-N1</td>
<td>1.283(2)</td>
</tr>
<tr>
<td>5</td>
<td>C1-N1</td>
<td>1.2817(17)</td>
</tr>
</tbody>
</table>

The bond angles between the equatorial fluorine atoms, the sulfur atom, and the axial fluorine atom of each compound are slightly smaller than 90°. Perhaps the bond shortening is related to the crystal packing of the compounds. The longer equatorial sulfur to fluorine bonds are localized to a region of space that other molecular units cannot conceivably occupy. However, the equatorial fluorine atoms with shorter bond lengths do occupy a region of space which can be occupied by other molecular units. This behavior can possibly be explained by Bent’s rule. The rule states: “Atomic s-character tends to
concentrate in orbitals that are directed toward electropositive groups and atomic p-character tends to concentrate in orbitals that are directed toward electronegative groups. As the sulfur to fluorine bonds should have bonding orbitals with greater p-character than the bonding orbitals comprising the sulfur to nitrogen bonds in compounds 1-5, this will lead to smaller axial fluorine atom to sulfur atom to equatorial fluorine atom bond angles.

Compounds 4 and 5 both feature a saturated five-membered carbonate ring, which is non-planar in configuration. In both compounds, the ring is observed to have a twisted conformation, rather than an envelope or planar conformation. The cause for the conformation that is observed for the five-membered rings may be the SF₅N- functional group bonded to the carbon atom at the “2” position of the ring. The twist angle (T= 30.07°) of compound 4 is larger than that of compound 5 (T= 21.49°). This may be due to the higher steric hindrance of the methyl substituents of compound 4. In comparison, 1,3-benzothiazolone and 1,3-benzoazol-2(3H)-one both have structures in which each atom lies within a single plane in space.

In the long-range packing structures of fluorine-containing molecules, it has been known that the fluorine-containing phases tend to segregate from the non-fluorine-containing phases. The same phenomenon that fluorine-containing phases and non-fluorine-containing phases exhibit an alternating arrangement is observed in the long-range packing structure of each crystal as well, as shown in Figure 2.4.
Figure 2.4. Fluorine-containing and non-fluorine-containing phases segregation of compound 1-5. Green-F, blue-N, yellow-S, red-O, grey-C, and white-H.

In the packing structures of compounds 1-5, several types of short contacts were observed. In 2011, an IUPAC definition and a list of criteria pertaining to the hydrogen bond was given. In the cited work it is stated: “The length of the short contact relative to the sum of the van der Waals radii of a hydrogen atom and the acceptor atom is not the sole criterion for determining the presence of a hydrogen bond. Additionally, the angle between X-H···Y, where X is an atom that the hydrogen atom is bonded to, and Y is a more electronegative element than hydrogen, should be linear.” From this definition, hydrogen bonds (H-bond) including the H···N bond, H···O bond, and H···F bond were measured in each crystal structure, and these short contacts are listed in Table 2.5. Preferably, the bond angles of the hydrogen-bonded atoms are greater than 120 °, and all
the listed angles are above 120 ° except for the C2-H2A···F3 bond angle in compound 5 at 106.27 °.

Table 2.5. Intermolecular hydrogen bonds-short contact distances and angles.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N1···H2</td>
<td>2.200</td>
<td>N2-H2···N1 = 165.5</td>
</tr>
<tr>
<td></td>
<td>F2···H7</td>
<td>2.628</td>
<td>C7-H7···F2 = 133.3</td>
</tr>
<tr>
<td></td>
<td>F5···H7</td>
<td>2.608</td>
<td>C7-H7···F5 = 139.2</td>
</tr>
<tr>
<td></td>
<td>F5···H2</td>
<td>2.659</td>
<td>N2-H2···F5 = 139.0</td>
</tr>
<tr>
<td></td>
<td>F4···H5</td>
<td>2.619</td>
<td>C5-H5···F4 = 151.2</td>
</tr>
<tr>
<td>2</td>
<td>N1···H4</td>
<td>2.590</td>
<td>C4-H4···N1 = 155.14</td>
</tr>
<tr>
<td></td>
<td>H5···F2</td>
<td>2.589</td>
<td>C5-H5···F2 = 128.98</td>
</tr>
<tr>
<td>3</td>
<td>H2···N1</td>
<td>1.974</td>
<td>N2-H2···N1 = 165.87</td>
</tr>
<tr>
<td></td>
<td>F2···H4</td>
<td>2.582</td>
<td>C4-H4···F2 = 130.45</td>
</tr>
<tr>
<td></td>
<td>H7···F3</td>
<td>2.649</td>
<td>C7-H7···F3 = 133.73</td>
</tr>
<tr>
<td>4</td>
<td>H4B···F3</td>
<td>2.572</td>
<td>C4-H4B···F3 = 141.2</td>
</tr>
<tr>
<td></td>
<td>H4A···F2</td>
<td>2.560</td>
<td>C4-H4A···F2 = 158.7</td>
</tr>
<tr>
<td></td>
<td>H6A···F5</td>
<td>2.560</td>
<td>C6-H6A···F5 = 165.9</td>
</tr>
<tr>
<td></td>
<td>F1···H6B</td>
<td>2.611</td>
<td>C6-H6B···F1 = 135.8</td>
</tr>
<tr>
<td>5</td>
<td>O1···H2A</td>
<td>2.628</td>
<td>C2-H2A···O1 = 124.77</td>
</tr>
<tr>
<td></td>
<td>H2B···O2</td>
<td>2.648</td>
<td>C2-H2B···O2 = 127.60</td>
</tr>
<tr>
<td></td>
<td>H3A···O2</td>
<td>2.638</td>
<td>C3-H3A···O2 = 121.09</td>
</tr>
<tr>
<td></td>
<td>F5···H3B</td>
<td>2.607</td>
<td>C3-H3B···F5 = 129.92</td>
</tr>
<tr>
<td></td>
<td>F3···H2A</td>
<td>2.626</td>
<td>C2-H2A···F3 = 106.27</td>
</tr>
<tr>
<td></td>
<td>F1···H3A</td>
<td>2.625</td>
<td>C3-H3A···F1 = 140.52</td>
</tr>
</tbody>
</table>
The nonlinear contacts can be considered incidental. Hydrogen bond N1···H2 (2.200 Å) of compound 1 and H2···N1 (1.974 Å) of compound 3 are the shortest among all the hydrogen bonds. It is also notable that both hydrogen atoms of N1···H2 and H2···N1 are covalently bonded to nitrogen atoms, while the H-bond acceptors are both imino nitrogen atoms, and their bond angles are the closest to 180°.

It is unknown if the SF₅ group bonded to the imino nitrogen atoms of both compounds plays a role in the hydrogen bonding described. However, previously shown, fluorine is less likely to form hydrogen bonds than nitrogen or oxygen.²⁶ For compounds 1 and 3, which both have a secondary amine, it is much more likely for the interaction of the hydrogen atom of the secondary amine to interact with the imino group of the compound. Besides the H-bonding, contact distances involving fluorine atoms and another non-hydrogen atom were observed as well. According to the IUPAC definition of a halogen bond, “A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.” A facet of atoms involved in intermolecular halogen bonding is that the distance of the bond is less than that of the sum of the van der Waals radii of the two atoms involved. Interestingly, short F···F contacts were observed in all five compounds as listed in Table 2.6. Each of these contacts involves fluorine atoms that are bonded to sulfur atoms, and the distances of these interactions are less than the sum of the van der Waals radii of two fluorine atoms. Due to the non-linear bond angles of the contacts observed in compounds 1-5, they may be considered Type 1 contacts. These types of interactions have been noted to be particularly weak and are usually observed to be incidental. The strength of the contacts observed for compounds 1-5 cannot be determined without further study. Notably, no axial fluorine atom to axial
fluorine atom interactions are observed. The cause of this may be due to the environment of the axial fluorine atom in the pentafluorosulfanyl group. This position may prevent one of the axial fluorine atoms from having an electrophilic region. Previous studies of fluorine to fluorine short contacts that have been used to compare other fluorine to fluorine interactions are of limited use to the interactions observed for compounds 1-5.

Table 2.6. F···F non-covalent interaction distances and angles.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Non-covalent interaction</th>
<th>Interaction length (Å)</th>
<th>Interaction angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>F5···F5</td>
<td>2.658</td>
<td>S1-F5···F5 = 134.2(2)</td>
</tr>
<tr>
<td>2</td>
<td>F1···F1</td>
<td>2.946</td>
<td>S1-F1···F1 = 118.76(4)</td>
</tr>
<tr>
<td>3</td>
<td>F1···O1</td>
<td>2.982</td>
<td>S1-F1···O1 = 157.0(1)</td>
</tr>
<tr>
<td></td>
<td>F3···F4</td>
<td>2.930</td>
<td>S1-F3···F4 = 132.7(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>S1-F4···F3 = 119.6(1)</td>
</tr>
<tr>
<td></td>
<td>F4···F2</td>
<td>2.947</td>
<td>S1-F2···F4 = 134.1(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>S1-F4···F2 = 120.6(1)</td>
</tr>
<tr>
<td></td>
<td>F5···F2</td>
<td>2.795</td>
<td>S1-F2···F5 = 135.7(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>S1-F5···F2 = 141.5(1)</td>
</tr>
<tr>
<td></td>
<td>F5···O1</td>
<td>2.837</td>
<td>S1-F5···O1 = 137.3(1)</td>
</tr>
<tr>
<td>4</td>
<td>F4···F4</td>
<td>2.857</td>
<td>S1-F4···F4 = 149.56(8)</td>
</tr>
<tr>
<td>5</td>
<td>F3···F3</td>
<td>2.977</td>
<td>S1-F3···F3 = 107.45(4)</td>
</tr>
<tr>
<td></td>
<td>F5···F1</td>
<td>2.765</td>
<td>S1-F5···F1 = 120.83(5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>S1-F1···F5 = 146.69(5)</td>
</tr>
<tr>
<td></td>
<td>O1···F2</td>
<td>2.987</td>
<td>S1-F2···O1 = 149.94(5)</td>
</tr>
</tbody>
</table>
2.4 Conclusions

The synthesis of SF₅NC-containing heterocycles has been shown, and the heterocycles have various and diverse heteroatoms at the “1” and “3” positions. The newly formed compounds are air stable, and single crystals of the compounds have been grown and studied by X-ray crystallography. A $^{19}$F NMR study of the compounds show that the identity of the heteroatoms that comprise the heterocyclic component of each structure may influence the chemical shift of the peaks in the spectrum. Using X-ray diffraction, hydrogen bonding interactions can be observed, including interaction between the fluorine atoms and methyl hydrogen atoms in compound 4. X-ray diffraction also reveals that bond angles between the axial and equatorial fluorine atoms of the SF₅ group are less than 90°, that can likely be explained by Bent’s rule and steric effects. Several preliminary reactions have been attempted with compounds 1 and 2. Compound 1 was mixed with 1-bromobutane and a base in dichloromethane. When sodium methoxide was used, no reaction was observed. The status of the reaction was monitored by $^{19}$F NMR spectroscopy. However, when DBU was used as a base, two distinct AB₄ patterns were observed in the $^{19}$F NMR spectrum of the reaction mixture. From this observation, it would seem that a reaction occurred to transform compound 1, and the SF₅ group remained intact throughout the reaction. The reaction product was un-isolable, though. Compound 2 was mixed with dodecylamine in a solution of dichloromethane at room temperature. The $^{19}$F NMR spectrum of the reaction mixture revealed two distinct AB₄ patterns. This would seem to indicate that a reaction took place, and that the reaction product contains an SF₅ group. The product of this reaction was also un-isolable. The reaction chemistry of these heterocycles has yet to be explored fully, and this avenue may yield further utility for these heterocycles.
2.5 References


12. Grimm, H. G. On the systematic arrangement of chemical compounds from the perspective of research on atomic composition; and on some challenges in experimental chemistry. *Naturwissen Schaffen* 1928, 17, 557-564.


CHAPTER THREE

SYNTHESIS OF SF5CF2-CONTAINING QUINAZOLINONES

3.1 Introduction

Molecules containing a quinazoline structure are often prized for their antibacterial, anti-inflammatory, and analgesic properties.\textsuperscript{1} Several synthetic paths to non-fluorine-containing quinazolinones have been described in recent years, and often metallic catalysts are needed in these methods.\textsuperscript{2} Fluorine as a substituent in heterocycles has attracted wide interest, but posed great challenges to chemists due to the limited availability of a convenient fluorine source. Several trifluoromethyl-containing quinazolinones illustrated in Figure 3.1 have been synthesized, and their medicinal properties have been shown to be promising. The quinazolinone 2-quinazolin-4-one was first reported in 1969 and patented as a herbicidal compound in 1972.\textsuperscript{3}

Thymidylate synthase inhibitors have been used as antitumor compounds since the discovery of 5-fluorouracil, compound \textit{a}, shown in Figure 3.1.\textsuperscript{4,5} These compounds block the enzyme thymidylate synthase from converting deoxyuridine monophosphate to deoxythymidine monophosphate. By decreasing the production of deoxythymidine monophosphate in tumor cells, an imbalance results in the nucleotides in the cell, along with increased amounts of deoxyuridine monophosphate, and DNA damage occurs. This DNA damage ultimately leads to the death of the tumor cell. One compound that was tested for its ability as an antifolate thymidylate synthase inhibitor was the glutamic acid derivative compound \textit{b} shown in Figure 3.1.\textsuperscript{6} Upon testing, the compound was found to be an effective thymidylate synthase inhibitor.
A second application of quinazolinones is their usage as angiotensin converting enzyme (ACE) inhibitors.

Figure 3.1. Examples of previously reported F-containing and CF$_3$-containing quinazolinones.$^{3b,4-7}$

The enzyme angiotensin II is responsible for increasing blood pressure in the body. Angiotensin converting enzyme inhibitors prevent angiotensin I from being converted to angiotensin II. This disruption of the angiotensin system relaxes blood vessels throughout
the body, lowering blood pressure. Testing of compound c illustrated in Figure 3.1 as an ACE inhibitor demonstrated the potency of this compound.7

Recently, a series of trifluoromethylated quinazolin-4(3H)-ones such as compound d illustrated in Figure 3.1 were successfully synthesized using trifluoroacetic acid (TFA) as a source of the trifluoroacetate group, which largely enriched the category of F-containing quinazolinones. This work is encouraging due to the one-pot synthetic style and the great availability of the CF3 source TFA.3b However, the pentafluorosulfanyl (SF5) moiety has not been as available as other fluorine-containing synthons due to the difficulty of synthesizing and handling the SF5-containing building blocks.

In this work, the quinazolinones presented herein were synthesized using SF5CF2C(O)Cl as the source of the SF5CF2 group, and no quinazolinones containing the SF5CF2 moiety have been reported previously. Earlier studies have shown that SF5CF2C(O)Cl reacts with primary amines in order to form amides.8 Cyclization of quinazolinone precursors was attempted by refluxing the SF5CF2-containing amides in glacial acetic acid.9 This approach has been used with various substrates. Cyclization of starting 1,2-diamides could also be achieved by refluxing them in a solution of strong base.10 Either technique can produce a quinazolin-4(3H)-one from an o-amidoamide. Besides the synthetic work, several crystal structures were successfully solved using single crystal X-ray diffraction. Among these structures, a variety of both hydrogen bonding and fluorine-fluorine short contact distances were observed. Structure elucidation was also performed using 1H, 19F, and 13C NMR spectroscopy, along with ATR-IR spectroscopy and high-resolution mass spectrometry.
3.2 Experimental

3.2.1 Materials

3-Aminobenzofuran-2-carboxamide was purchased from Chem-Impex International, Inc., while 5-chloro-2-nitrobenzamide, 5-methyl-2-nitrobenzamide, triethylamine, piperonylic acid, 2-aminothiophene-3-carboxamide, triethylamine, sodium hydride, and pyridine were purchased from Sigma-Aldrich. Argon was purchased from Airgas. 5-Chloro-2-aminobenzamide, 5-methyl-2-aminobenzamide, and 6-amino-1,3-benzodioxole-5-carboxamide were synthesized by literature procedures. Triethylamine was distilled from phosphorus pentoxide and stored over 4 Å molecular sieves. All other reagents were used as purchased. All reactions were carried out in either 316 stainless steel Hoke® cylinders or in Pyrex glassware.

All $^{19}$F NMR (283 MHz), $^1$H NMR (300 MHz), and $^{13}$C NMR (75.5 MHz) spectra were recorded on a JEOL ECX-300 NMR spectrometer. The abbreviations used to describe signal multiplicity in NMR spectroscopy are as follows: s-singlet, bs-broad singlet, d-doublet, t-triplet, qn-quintet, m-multiplet. Chemical shifts (δ) are presented in ppm downfield from DMSO-$d_6$, CDCl$_3$, or acetone-$d_6$ for $^1$H NMR and from CCl$_3$F for $^{19}$F NMR spectroscopy, respectively. The ATR-IR spectra were recorded on a Nicolet iS5 FT-IR spectrometer with an iD5 ATR-IR accessory, with a resolution of +/-4 cm$^{-1}$. High-resolution mass spectrometry analyses were carried out at The University of Alabama (Tuscaloosa, AL), using a Waters AutoSpec-Ultima NT sector mass spectrometer. Single crystal X-ray data was collected on a Bruker D8 Venture instrument. The structures were solved and refined by using full-matrix least-squares on F$^2$ method with Bruker SHELXTL software.

Note: Compounds numbered with the letter Q (e.g. Compound Q1) contain a quinazolinone moiety.
3.2.2 Synthesis of 2-[(2,2-difluoro-2-pentafluorosulfanylacetyl)amino]-5-methylbenzamide (Compound 6)

To a two-necked, 100-mL round-bottomed flask, equipped with a PTFE-coated magnetic stir bar, septum, and a Kontes® valve adaptor, 0.12 g (0.76 mmol) of 5-methyl-2-aminobenzamide was added. The flask was evacuated on the vacuum line overnight. Next, 10 mL of anhydrous THF was injected into the flask. An amount of 0.18 g (0.77 mmol) of SF$_5$CF$_2$C(O)Cl was condensed into the flask. The flask was held at -78 °C for 30 minutes, while the contents were stirred. Sequentially, 0.08 mL (1 mmol) of anhydrous pyridine was slowly dripped into the flask. The flask was then warmed slowly to ambient temperature, and the reaction mixture allowed to stand overnight with stirring. The product was extracted with ethyl acetate. After extraction, the organic layer was dried over MgSO$_4$, filtered, and concentrated via a rotary evaporator. The concentrated material was recrystallized from acetone. The yield is 37%, 0.10 g (0.28 mmol) of product was recovered. The melting point of this compound was not measured. $^{19}$F NMR (acetone-$d_6$, 283 MHz) δ 66.56 (qn, 1F), 39.81 (dt, 4F, 144 Hz), -88.90 (qn, 2F, 11.3 Hz). $^1$H NMR (acetone-$d_6$, 300 MHz). δ 1.199-1.238 (m), 2.422 (s), 7.551 (s), 7.581 (s), 7.655 (d), 7.685 (d), 7.708 (s). ATR-IR (film)1672 (m), 1618 (w), 1487 (w), 1343 (w), 1300 (w), 1250 (w), 1214 (w), 1155 (w), 1133 (w), 1019 (w), 936 (w), 905 (w), 826 (s), 781 (m), 724 (w), 695 (m), 672 (w), 636 (w), 589 (w), 567 (w), 537 (w) cm$^{-1}$.

3.2.3 Synthesis of 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1)

To a one-necked, 50-mL round-bottomed flask, equipped with a PTFE-coated stir bar, 0.10 g (0.28 mmol) of compound 6$^{10}$ was added. Next, an amount of 10 mL of glacial
acetic acid and 4 mL of acetic anhydride were added to the flask. A water-jacketed reflux condenser was placed atop the flask, and the solution was refluxed for 24 hours. Once 24 hours had passed, the volatile fraction of the reaction mixture was evaporated from the flask using a rotary evaporator, and the crude organic material was extracted with ethyl acetate. The organic layer was dried over MgSO₄, the MgSO₄ was filtered off, and the organic solution concentrated using a rotary evaporator. The crude crystals were recrystallized using acetone. The yield is 10%, and 0.0094 g (0.028 mmol) of product was recovered. The compound decomposes as well as melts at 208-210 °C, which was measured in a sealed capillary. 

\[ ^{19}F\text{ NMR (CDCl}_3/DMSO-d_6, 283 MHz) \delta 65.46 (qn, 1F,) \]
\[ 40.31 \text{ (dt, 4F, 144 Hz), -88.25 (qn, 2F, 11.3 Hz).} \]
\[ ^1H\text{ NMR (CDCl}_3/DMSO-d_6, 300 MHz) \delta 1.722-1.775 \text{ (m), 6.898-6.965 \text{ (m), 7.233 \text{ (s), 7.263 \text{ (s).}} \]
\[ ^{13}C\text{ NMR (CDCl}_3/DMSO-d_6, 75 MHz) \delta 126.3 \text{ (s), 126.4 \text{ (s), 128.8 \text{ (s), 136.7 \text{ (s), 137.0 \text{ (s), 140.2 \text{ (s), 145.4 \text{ (s), 146.3 \text{ (s), 160.9 \text{ (s), 162.4 \text{ (s). \}} \]
\[ \text{ATR-IR (film) 1674 \text{ (s), 1630 \text{ (w), 1619 \text{ (w), 1505 \text{ (vw), 1487 \text{ (m), 1342 \text{ (w), 1316 \text{ (w), 1300 \text{ (w), 1251 \text{ (m), 1214 \text{ (w), 1233 \text{ (s, 1199 \text{ (m), 1155 \text{ (m), 1133 \text{ (m), 1089 \text{ (m), 1018 \text{ (s, 936 \text{ (m), 906 \text{ (m), 844 \text{ (s, 797 \text{ (s, 781 \text{ (s, 724 \text{ (m), 696 \text{ (s), 672 \text{ (m), 635 \text{ (m), 614 \text{ (w), 590 \text{ (m), 568 \text{ (m cm}^{-1}. \]}
\[ \text{HRMS (EI) mass calculated for (C}_{10}H_7N_2OF_7S) \text{calcd.: 336.0167, found: 336.0177.} \]

3.2.4 **Synthesis of 5-chloro-2-[(2,2-difluoro-2-pentafluorosulfanyl-acetyl)amino]-benzamide (Compound 7)**

To a one-necked, 50-mL round-bottomed flask, equipped with a PTFE-coated stir bar, 0.77 g (4.5 mmol) of 5-chloro-2-aminobenzamide was added, in a dry box. The flask was fitted with a septum and moved from the dry box to a fume hood. The flask was placed on a magnetic stir plate, and 10 mL of anhydrous THF was added to the flask via syringe. A latex balloon filled with argon was connected to the flask. Next, 0.41 mL (4.5 mmol) of pyridine was added to the flask via syringe. At this point, the flask was cooled to -78 °C.
To the flask, 7.2 mL of a 0.62 M solution of SF₂CF₂C(O)Cl in anhydrous THF was added dropwise. Once the solution had been fully added, the contents of the flask were stirred, and the flask was slowly warmed to room temperature. Once the flask reached room temperature, the reaction mixture was stirred overnight. After the reaction mixture had been stirred, the mixture was filtered using filter paper. The flask with the filtered solution was then connected to a rotary evaporator, and the volatile components were evaporated. The crude solid was extracted using dichloromethane and water. The organic layer was dried over MgSO₄, and the solvent re-evaporated. The solid product was then purified by silica gel chromatography. The eluent used was an 80:20 solution of hexanes and ethyl acetate. The fractions containing product were then collected, and the eluent evaporated. The crude product was finally isolated by crystallization using a 50:50 mixture of hexanes and acetone. The yield is 14%, and 0.24 g (0.63 mmol) of product was collected. The melting point is 240 °C. ¹⁹F NMR (CDCl₃/DMSO-d₆, 283 MHz) δ 67.96 (qn, 1 F), 41.17 (dt, 4 H, 147 Hz), -87.65 (qn, 2 F, 11.3 Hz). ¹H NMR (CDCl₃/DMSO-d₆, 300 MHz) δ 11.30 (s), 11.17 (s), 8.077 (s), 7.970 (s), 7.777-7.772 (m), 7.452 (dd) 7.100 (d). ¹³C NMR (CDCl₃/DMSO-d₆, 75 MHz) δ 115.8 (s), 121.7 (s), 123.8 (s), 128.6 (s), 132.7 (s), 133.6 (s), 143.7 (s), 159.3 (s), 160.4 (s). ATR-IR (film)2775 (w), 1682 (s), 1629 (w), 1606 (w), 1516 (w), 1467 (m), 1424 (w), 1337 (w), 1315 (w), 1285 (w), 1258 (w), 1228 (w), 1208 (s), 1159 (w), 1132 (w), 1115 (w), 1020 (w), 934 (m), 893 (w), 858 (s), 848 (s), 823 (s), 792 (m), 775 (s), 704 (m), 676 (w), 665 (m), 634 (m), 612 (w), 590 (m), 570 (w), 563 (m), 538 (w) cm⁻¹.

3.2.5 Synthesis of 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2)

To a one-necked, 10-mL round-bottomed flask, equipped with a PTFE-coated stir bar, 0.22 g (0.59 mmol) of compound 7 was added. Next, an amount of 5 mL of glacial
acetic acid was added to the flask. A water-jacketed reflux condenser was placed atop the flask, and the solution was refluxed for 24 hours. Once 24 hours had passed, the solution was removed using a rotary evaporator, and the organic products was re-dissolved in acetone. The organic layer was dried over MgSO₄, the MgSO₄ was filtered off, and the organic solution was concentrated using a rotary evaporator. The crude crystals were recrystallized using acetone. The yield is 72%, and 0.15 g (0.42 mmol) of product was recovered. The decomposition and melting point are 258-260 °C, which was measured in a sealed capillary. ¹⁹F NMR (CDCl₃/DMSO-d₆, 283 MHz) δ 67.66 (qn, 1F), 40.84 (dt, 4F, 144 Hz), -87.41 (qn, 2F, 12.7 Hz). ¹H NMR (CDCl₃/DMSO-d₆, 300 MHz) δ 8.986 (s), 8.612 (d), 8.564 (d), 8.417 (d), 8.388 (d), 8.348 (s), 8.337 (s), 8.319 (s), 8.309 (s), 8.221 (s), 8.191 (s). ¹³C NMR (CDCl₃/DMSO-d₆, 75 MHz) 123.9 (s), 125.6 (s), 125.7 (s), 127.0 (s), 130.7 (s), 132.8 (s), 134.5 (s), 135.4 (s), 135.6 (s). ATR-IR (film) 2772 (w), 1679 (m), 1627 (w), 1606 (w), 1506 (w), 1467 (m), 1425 (w), 1337 (w), 1316 (w), 1285 (w), 1259 (w), 1228 (w), 1208 (m), 1159 (w), 1131 (w), 1115 (w), 1019 (w), 933 (w), 894 (w), 857 (s), 847 (s), 822 (s), 775 (s), 704 (m), 676 (m), 664 (m), 634 (m), 612 (w), 588 (m), 564 (m), 537 (m) cm⁻¹. HRMS (EI) mass calculated for \( \text{C}_9\text{H}_4\text{N}_2\text{OF}_7\text{SCl} \) calcd.: 355.9621, found: 355.9613.

3.2.6 Synthesis of 6-[[difluoro(pentafluorosulfanyl)acetyl]amino]-1,3-benzodioxole-5-carboxamide (Compound 8)

To a one-necked, 50-mL round-bottomed flask, equipped with a PTFE-coated stir bar, 0.31 g (1.7 mmol) of 6-amino-1,3-benzodioxole-5-carboxamide was added, in a dry box. The flask was fitted with a septum and moved from the dry box to a fume hood. The flask was placed on a magnetic stir plate, and 10 mL of anhydrous THF was added to the flask via syringe. A latex balloon filled with argon was connected to the flask. Next, 0.14 mL (1.7 mmol) of pyridine was added to the flask via syringe. At this point, the flask was
cooled to -78 °C. To the flask, 2.7 mL of a 0.62 M solution of SF₅CF₂C(O)Cl in anhydrous THF was added to the flask dropwise. After the solution had been added to the flask, the contents of the flask were stirred, and the flask was warmed up to room temperature. The contents of the flask were stirred for another 24 hours. Once the stirring was completed, the solid components of the reaction mixture were filtered out from the reaction solution. The solid components of the reaction mixture were washed with ethyl acetate, and the ethyl acetate was filtered again. The washings were combined with the filtered reaction solvent, and the solvent was evaporated via a rotary evaporator. The organic solid left behind was extracted with ethyl acetate. The organic layer was dried over MgSO₄, filtered, and the solvent re-evaporated. The crude solid was then purified using silica gel chromatography, with an eluent of 80:20 hexanes to ethyl acetate. The fractions which contained product were collected and combined. The eluent was evaporated, leaving behind a solid product. The product was isolated via crystallization. The solvent system for this process was a solution of 90% hexanes, 10% ethyl acetate. The yield is 9.3%, and 0.061 g (0.16 mmol) of product was recovered. The decomposition temperature is 208-210 °C with melting. A flame sealed capillary was used to measure the melting point. ¹⁹F NMR (CDCl₃/DMSO-d₆, 283 MHz) δ 67.62 (qn, 1F), 39.82 (dt,4 F, 144 Hz), -87.41 (qn, 2 F, 14.1 Hz). ¹H NMR (CDCl₃/DMSO-d₆, 300 MHz) 6.254-6.278 (m), 7.174 (s), 7.223-7.268 (m), 7.479 (s), 7.603 (d), 7.634 (d), 7.852 (bs), 11.13 (bs). ¹³C NMR (CDCl₃/DMSO-d₆, 75 MHz) 102.0 (s), 103.4 (s), 106.8 (s), 126.3 (s), 134.8 (s), 149.8 (s), 154.5 (s). ATR-IR (film) 2915 (w), 1709 (w), 1670 (m), 1621 (w), 1591 (w), 1504 (w), 1463 (m), 1438 (w), 1396 (w), 1376 (w), 1316 (w), 1273 (m), 1221 (m), 1208 (m), 1164 (w), 1145 (w), 1115 (w), 1051 (w), 1038 (m), 1018 (w), 946 (w), 921 (m), 872 (m), 853 (s), 819 (s), 788 (m), 775 (m), 752 (m), 719 (w), 703 (m), 673 (w), 661 (m), 623 (w), 615 (w), 602 (w), 582 (m), 568 (m), 534 (w) cm⁻¹.
3.2.7 Synthesis of 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinoxalin-8(7H)-one (Compound Q3)

To a one-necked, 10-mL round-bottomed flask, equipped with a PTFE-coated stir bar, 0.06 g (0.16 mmol) of compound 8 was added. Next, an amount of 5 mL of glacial acetic acid was added to the flask. A water jacketed reflux condenser was placed atop the flask, and the solution was refluxed for 24 hours. Once 24 hours had passed, the solution was evaporated from the flask using a rotary evaporator, and the organic products were recrystallized from acetone. The yield is 85%, and 0.05 g (0.14 mmol) of product was recovered. The decomposition temperature is 220 °C, with melting. A flame sealed capillary was used to measure the melting point. $^{19}$F NMR (CDCl$_3$/DMSO-d$_6$, 283 MHz) δ 67.54 (qn, 1 F), 40.56 (dt, 4 F, 144 Hz), -88.11 (qn, 2 F, 14.1 Hz). $^1$H NMR (CDCl$_3$/DMSO-d$_6$, 300 MHz) 5.806-5.285 (m), 6.798-6.785 (m), 7.142-7.129 (m), 7.269-7.257 (m). $^{13}$C NMR (CDCl$_3$/DMSO-d$_6$, 75 MHz) δ 102.6-102.7 (m), 106.3 (s), 149.2 (s), 153.8 (s). ATR-IR (film) 2915 (w), 1670 (m), 1623 (w), 1591 (w), 1504 (w), 1463 (m), 1438 (w), 1396 (w), 1316 (w), 1273 (w), 1222 (m), 1209 (m), 1164 (w), 1115 (w), 1038 (m), 1018 (w), 946 (w), 921 (w), 872 (w), 854 (m), 821 (m), 788 (m), 756 (w), 718 (w), 703 (w), 674 (w), 623 (w), 616 (w), 602 (w), 580 (w), 536 (w), 527 (m).

3.2.8 Synthesis of 2-[2,2-difluoro(pentafluorosulfanyl)acetamide] benzamide (Compound 9)

To a 10-mL, flame dried round-bottomed flask, equipped with a magnetic stir bar, 0.14 g (1.4 mmol) of 2-amino benzamide was added. The flask was topped with a rubber septum, and a latex balloon filled with nitrogen was connected to the flask. A 2-mL of dichloromethane along with 0.17 mL (1.2 mmol) of triethylamine were added to the flask successively, and the reaction mixture was stirred. The reaction mixture was cooled to 0 °C and 0.29 g (1.2 mmol) of pentafluorosulfanyldifluoroacetyl chloride was added dropwise.
to the flask, with vigorous stirring. The reaction mixture was stirred for approximately 2
hours, and then it was slowly warmed up to room temperature. The reaction mixture was
stirred overnight, and 1 mL of a 10% HCl solution was added to the reaction mixture. The
solvent was then evaporated. The residue was purified from an 80:20 mixture of hexanes
and ethyl acetate. The yield is 64%, and 0.26 g (0.77 mmol) of product was recovered.
The melting point of the compound was not measured. $^{19}$F NMR (Acetonitrile-$d_5$, 283 MHz)
$\delta$ 66.39 (qn, 1F), 40.54 (dt, 4 F, 144 Hz), -92.23 (qn, 2F, 12.7 Hz). $^1$H NMR (Acetonitrile-
$d_5$, 300 MHz) 8.480 (dd, $^2$J = 8.4 Hz, $^3$J = 0.6 Hz), 7.776 (dd, $^2$J = 8.1 Hz, $^3$J = 1.2 Hz),
7.597 (td, $^2$J = 8.7 Hz, $^3$J = 1.2 Hz) 7.281 (td, $^2$J = 7.8 Hz, $^3$J = 1.2 Hz) 7.206 (s),
6.514 (bs). $^{13}$C NMR (acetonitrile-$d_5$, 75 MHz) $\delta$ 117.4 (s), 120.7 (s), 125.0 (s), 128.6 (s),
133.5 (s), 138.2 (s), 154.6 (t, $^2$J = 24.9 Hz), 171.23 (s).

3.2.9 Synthesis of 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one
(Compound Q4)

To a one-necked, 50-mL round-bottomed flask, equipped with a PTFE-coated stir
bar, 0.10 g (0.28 mmol) of compound 9 was added. Next, 10 mL of glacial acetic acid and
4 mL of acetic anhydride were added to the flask. A water jacketed reflux condenser was
placed atop the flask, and the solution was refluxed for 24 hours. Once 24 hours had
passed, the solution was evaporated from the flask using a rotary evaporator, and the
organic products were extracted with ethyl acetate. The organic layer was dried over
MgSO$_4$, the MgSO$_4$ was filtered off, and the organic solution was concentrated using a
rotary evaporator. The crude crystals were recrystallized using acetone. The yield is 73%,
and 0.064 g (0.20 mmol) of product was recovered. The melting point of the compound
was not measured. $^{19}$F NMR (acetone-$d_6$, 283 MHz) $\delta$ 67.61 (qn, 1 F),
40.92 (dt, 4 F, 144 Hz), -87.77 (qn, 2 F, 14.1 Hz). $^1$H NMR (acetone-$d_6$, 300 MHz) $\delta$ 7.693
(td, $^2$J = 7.5 Hz, $^3$J= 0.9 Hz) 7.823 (s), 7.848 (s), 7.934 (td, $^2$J = 8.4 Hz, $^3$J= 1.4 Hz),
8.255 (dd, $^2J = 7.8$ Hz, $^3J = 1.1$ Hz). $^{13}$C NMR (acetone-$d_6$, 75 MHz) δ 122.9 (s), 126.5 (s), 128.6 (s), 129.6 (s), 135.3 (s), 146.9 (s), 160.7 (s). HRMS (El) mass calculated for (C$_9$H$_7$N$_2$OF$_7$S) calcd.: 322.0011, found: 321.9999.

3.2.10 **Synthesis of 3-[2,2-difluoro(pentafluorosulfanyl)acetamido]-thiophene-2-carboxamide (Compound 10)**

To a 10-mL, flame dried round-bottomed flask equipped with a magnetic stir bar, 0.0263 g (1 mmol) of 95% sodium hydride was added in a dry box. To a second 10-mL, flame dried round-bottomed flask, 0.227 g (1.6 mmol) of 3-amino-thiophene-2-carboxamide was added in a dry box. Both flasks were topped with rubber septa and moved to a fume hood. A latex balloon filled with nitrogen was connected to the flask containing sodium hydride. To the flask containing 3-amino-thiophene-2-carboxamide, 2 mL of anhydrous DMF was added. The flask containing the sodium hydride was cooled to 0 °C, and the solution of 3-amino-2-carboxamide was slowly dripped into the flask containing sodium hydride. The reaction mixture was warmed up to room temperature and was stirred for 1 hour. Then, the reaction mixture was cooled to -10 °C, and 0.24 mL (1 mmol) of pentafluorosulfanyldifluoroacetyl chloride was added dropwise. The mixture was slowly warmed up to room temperature and was stirred overnight. Afterward, 5 mL of ethyl acetate and 2 mL of a 10% aqueous solution of NaHCO$_3$ were added to the reaction mixture successively. The organic layer was separated from the aqueous layer. Next, the aqueous solution was acidified to a pH between 3 and 4, and subsequently extracted with more ethyl acetate. The organic solutions were combined and dried over MgSO$_4$. After the organic fractions had been filtered and then evaporated, the crude product was recrystallized using benzene. The yield is 55%, and 0.19 g (0.55 mmol) of product was recovered. The melting point of the compound was not measured. $^{19}$F NMR
(acetone-$d_6$, 283 MHz) $\delta$ 66.27 (qn, 1 F), 40.66 (dt, 4 F, 147 Hz), -92.12 (qnd, 2 F, 12.7 Hz). $^1$H NMR (acetone-$d_6$, 300 MHz) $\delta$ 7.361 (bs, 2 H), 7.788 (d, $^2J = 5.7$ Hz, 1 H), 7.973 (d, $^2J = 5.4$ Hz, 1 H), 12.956 (s, 1 H).

$^{13}$C NMR (acetone-$d_6$, 75 MHz) $\delta$ 115.9 (s), 121.6 (s), 129.7 (s), 140.8 (s), 153.5 (t, $^2J = 25.9$ Hz), 166.0 (s).

3.2.11 Synthesis of 2-[difluoro(pentafluorosulfanyl) methyl] thieno [3,2-d] pyrimidin-4(3H)-one (Compound Q5)

To a one-necked, 50-mL round-bottomed flask equipped with a PTFE-coated stir bar, 0.10 g (0.28 mmol) of compound 10 was added. Next, an amount of 10 mL of glacial acetic acid and 4 mL acetic anhydride were added to the flask. A water-jacketed reflux condenser was placed atop the flask, and the solution was refluxed for 24 hours. Once 24 hours had passed, the solution was evaporated from the flask using a rotary evaporator, and the remaining organic products were extracted with ethyl acetate. The organic layer was dried over MgSO$_4$, filtered, and concentrated using a rotary evaporator. The crude crystals were recrystallized using acetone. The yield is 62%, and 0.057 g (0.17 mmol) of product was recovered. The melting point of the compound was not measured. No NMR or IR spectra were collected for this compound. HRMS (EI) mass calculated for (C$_7$H$_3$N$_2$OF$_7$S$_2$) calcd.: 327.9575, found: 327.9564.

3.2.12 Synthesis of 3-(pentafluorosulfanyl-difluoroacetylamino)-2-benzofuran-carboxamide (Compound 11)

To a 50-mL, three-necked round-bottomed flask, equipped with a PTFE-coated magnetic stir bar, a septum, a Kontes® valve adaptor, and a glass plug, 0.25 g (1.9 mmol) of 3-amino-2-benzofuran-carboxamide was added. The flask was evacuated on a vacuum
line overnight. Next, 10 mL of anhydrous THF was injected into the flask. The flask was frozen to -196 °C, and 0.39 g (1.4 mmol) of SF₅CF₂C(O)Cl was condensed in. The flask was held at -78 °C for 30 minutes while the contents were stirred. Additionally, a balloon filled with pure argon was connected to the flask. An amount of 0.11 g (1.5 mmol) of anhydrous pyridine was injected to the reaction mixture dropwise. The flask was then slowly warmed to room temperature, and the reaction mixture was stirred overnight. The THF was then evaporated by a rotary evaporator, and the organic product was extracted with ethyl acetate. The organic solution was washed three times with water, then the organic layer was separated, dried over MgSO₄, and evaporated. This crude residue was purified by silica gel chromatography (90:10 Hexane/EtOAc). The collected product was recrystallized in acetone, and then dried in a vacuum chamber for 24 hours. The yield is 90%, and 0.48 g (1.3 mmol) of product was collected. The melting point is 170-172 °C, and a flame sealed capillary was used to measure the melting point. ¹⁹F NMR (acetone-d₆, 283 MHz) δ 67.06 (qn, 1F), 41.98 (dt, 4F, 147 Hz), -90.62 (t, 2H, 11.3 Hz). ¹H NMR (acetone-d₆, 300 MHz) δ 2.81 (bs, 2H), 7.37-7.41 (m, 1H), 7.57-7.59 (d, 6 Hz, 2H), 8.31-8.34 (d, 9 Hz, 1H), 11.81 (s, 1H). ¹³C NMR (acetone-d₆, 75 MHz) δ 112.1 (s), 115.1 (s), 119.5 (s), 120.8 (s), 123.8 (s), 125.4 (s), 128.7 (s), 134.6 (s). ATR-IR (film): 3272 (w), 3081 (w), 2928 (w), 2360 (w), 2341 (w), 2227 (w), 1727 (m), 1618 (w), 1610 (w), 1591 (w), 1549 (m), 1480 (w), 1450 (w), 1366 (w), 1300 (w), 1249 (w), 1215 (m), 1194 (m), 1179 (m), 1154 (w), 1141 (w), 1107 (w), 1015 (w), 950 (w), 881 (m), 851 (m), 826 (s), 768 (w), 747 (s), 711 (m), 674 (m), 645 (m), 607 (m), 589 (w), 573 (m), 564 (w) cm⁻¹.
3.2.13 Synthesis of N-(2-cyano-3-benzofuran-2-yl)-2,2-difluoro-2-pentafluorosulfanylacetamide (Compound 12)

To a 50-mL, three-necked round-bottomed flask, equipped with a PTFE-coated magnetic stir bar, a septum, a Kontes® valve adaptor, and a glass plug, 0.20 g (1.1 mmol) of 3-aminobenzofuran-2-carboxamide was added. The flask was evacuated on a vacuum line overnight. Next, 20 mL of anhydrous CH₂Cl₂ was injected into the flask. The flask was frozen to -196 °C, and 0.26 g (1.1 mmol) of SF₅CF₂C(O)Cl and 0.17 g (1.7 mmol) of triethylamine were condensed in. The flask was held at -78 °C for 30 minutes while the contents of the flask were stirred. Additionally, a balloon filled with pure argon was connected to the flask. The flask was then slowly warmed to room temperature, and the reaction mixture was stirred overnight. The dichloromethane was then evaporated by a rotary evaporator, and the organic product was extracted with ethyl acetate. The organic solution was washed several times with water, then the organic layer was separated, dried over MgSO₄, filtered, and evaporated. The collected product was recrystallized in THF, and then dried in a vacuum chamber for 24 hours. The yield is 1.3%, and 5 mg of the product was recovered. The compound begins to sublime within a sealed tube at around 40 °C. "F NMR δ 65.46 (qn, 1F), 41.02 (dt, 4F, 144 Hz), -91.78 (qn, 2F, 14.1 Hz). ATR-IR (film) 2228 (vw), 1742 (w), 1732 (w), 1614 (w), 1519 (w), 1393 (w), 1256 (w), 1211 (w), 1202 (w), 1178 (w), 1153 (w), 1136 (w), 1102 (w), 894 (w), 863 (m), 830 (m), 811 (m), 751 (m), 711 (w), 671 (w), 660 (w), 635 (w), 593 (w), 587 (w), 576 (w), 559 (w) cm⁻¹. HRMS (EI) mass calculated for (C₁₁H₈N₂O₂F₇S) calcd.: 361.9960, found: 361.9966.

3.3 Results and Discussion

The SF₅CF₂-containing quinazolinones compounds Q1-Q5 illustrated in Scheme 3.1 were prepared in a two-step synthesis.
Scheme 3.1. Two-steps synthesis of SF₅CF₂-containing quinazolinones Q₁-Q₅.

The first step is to bond the SF₅CF₂C(O)- group to the amine group of the starting materials. Pyridine, triethylamine, and sodium hydride were successfully used as bases to accomplish the amidation of the amine group of the starting materials.¹³ The vicinal pentafluorosulfanyl difluoroacetoamide amide products from this reaction were then
cyclized to their corresponding quinazolinones using glacial acetic acid, and in the cases of compounds Q1, Q4, and Q5. The amidation of a 2-amino benzamide-type compound, followed by acidic or basic catalyzed cyclization is a common technique used to synthesize quinazolinones. While other techniques may potentially be used, the same technique was used to synthesize all the quinazolinones in Chapter 3. This route was chosen for several reasons. It is convenient for our group to use SF$_5$CF$_2$C(O)Cl, making it an ideal building block. The use of glacial acetic acid, sometimes with acetic anhydride added to solution, as a solvent and catalyst for the cyclization reactions helped to make these reactions’ set-up and purifications straightforward. When 2-amino-5-methyl benzamide, 2-amino-5-chlorobenzamide, and 6-amino-1,3-benzo-dioxole-5-carboxamide were mixed with SF$_5$CF$_2$C(O)Cl, pyridine was used exclusively as the base. The only SF$_5$CF$_2$-containing compounds recovered were the vicinal pentafluorosulfanyl difluoroacetoamide amides, compounds 6, 7, and 8, respectively. When 2-amino benzamide was mixed with SF$_5$CF$_2$C(O)Cl, the base used to drive the reaction forward was triethylamine. The product from this reaction was compound 9, a vicinal pentafluorosulfanyl difluoroacetoamide, produced in a 64% yield. This does not necessarily preclude the use of the base with some of the other starting materials, such as 2-amino-5-chloro benzamide, 2-amino-5-methyl benzamide, 3-aminothiophene-2-carboxamide, or 6-amino-1,3-benzodioxole-5-carboxamide. With regards to 3-aminothiophene-2-carboxamide, a sodium salt of the compound was generated by treating the compound with sodium hydride. When this sodium salt is mixed with SF$_5$CF$_2$C(O)Cl, compound 10, a pentafluorosulfanyl difluoroacetoamide benzamide is formed with a yield of 55%. Of the reactions discussed in the chapter, only compound 10 was synthesized using a sodium salt as a base. This technique can potentially be applied to the other starting materials. The reaction of SF$_5$CF$_2$C(O)Cl with
3-amino-2-benzofuran carboxamide is the only starting material with which different bases were utilized.

Pyridine and triethylamine were used as the bases for this reaction in separate attempts. When SF₅CF₂C(O)Cl was mixed with 3-amino-2-benzofuran carboxamide in the presence of pyridine, the vicinal pentafluorosulfanyldifluoroacetamino amide, compound 11, was recovered from the reaction. Changing the base from pyridine to triethylamine affected the product recovered from the reaction. With triethylamine as the base, compound 12 was recovered from the reaction mixture of SF₅CF₂C(O)Cl and 3-amino-2-benzofuran carboxamide. Compound 12 features a pentafluorosulfanyldifluoroacetamide group. However, the primary amide group of 3-amino-2-benzofuran carboxamide was dehydrated to a nitrile group. This reaction was only observed when SF₅CF₂C(O)Cl was mixed with 3-amino-2-benzofuran-carboxamide in the presence of triethylamine. The mechanism of this reaction is most likely a dehydration of the amide group. The reactions of SF₅CF₂C(O)Cl and 3-amino-2-benzofuran carboxamide are shown in Scheme 3.2.

When 3-aminobenzofuran-2-carboxamide was mixed with SF₅CF₂C(O)Cl and triethylamine, compound 12 was formed, though the yield was very low. The amine group of 3-aminobenzofuran-2-carboxamide reacted with SF₅CF₂C(O)Cl to form a SF₅CF₂-containing amide. The primary amide group of 3-aminobenzofuran-2-carboxamide was dehydrated to a nitrile. The choice of base when reacting 3-aminobenzofuran-2-carboxamide with SF₅CF₂C(O)Cl has a significant effect on the product that is produced.

The yields of compounds 6, 7, and 8 are not favorable, due to difficulties in isolating the reaction products. The isolation of compounds 7 and 8 were achieved by
recrystallization and column chromatography with various solvent systems. Compound 6 was isolated by recrystallization alone. Each of these compounds was found to have low solubility in organic solvents at room temperature, which complicated the isolation process for each compound. Compounds 6-10 were successfully cyclized by refluxing in glacial acetic acid, yielding the desired SF₅CF₂-containing quinazolinone compounds Q₁-Q₅. However, an attempt to cyclize compound 11 was not successful. The first attempt to cyclize compound 11 saw the compound mixed with refluxing glacial acetic acid for a period of 24 hours. This attempt to synthesize a cyclized compound was unsuccessful. An attempt to cyclize compound 11 using a longer reaction time of five days caused compound 11 to decompose.

Scheme 3.2. Synthesis of SF₅CF₂-containing benzofurans.

Each SF₅CF₂-containing compound exhibits a characteristic AB₄X₂ pattern of the SF₅CF₂-group in their ¹⁹F NMR spectra. The chemical shifts and coupling constants of all SF₅CF₂- moieties are listed in Table 3.1, and the chemical shifts of the fluorine atoms and coupling constants fall in the expected ranges.⁸,¹⁶
Table 3.1. $^{19}$F NMR spectral data for compounds 6-12 and Q1-Q4.

<table>
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<th>Compound</th>
<th>Axial Sulfur-Fluorine Atom Chemical Shift (PPM)</th>
<th>Equatorial Sulfur-Fluorine Atom Chemical Shift (PPM)</th>
<th>$^{2}$J$_{F}$ Coupling (Axial-Equatorial Fluorine) (Hz)</th>
<th>Carbon-Fluorine Atom Chemical Shift (PPM)</th>
<th>$^{3}$J$<em>{F}$ Coupling (Equatorial F-CF$</em>{2}$) (Hz)</th>
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<td>147</td>
<td>-87.65</td>
<td>11.3</td>
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<td>39.82</td>
<td>144</td>
<td>-87.41</td>
<td>14.1</td>
</tr>
<tr>
<td>9</td>
<td>66.39</td>
<td>40.54</td>
<td>144</td>
<td>-92.23</td>
<td>12.7</td>
</tr>
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<td>66.27</td>
<td>40.66</td>
<td>147</td>
<td>-92.12</td>
<td>12.7</td>
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<td>41.98</td>
<td>147</td>
<td>-90.62</td>
<td>11.3</td>
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<td>41.02</td>
<td>144</td>
<td>-91.78</td>
<td>14.1</td>
</tr>
<tr>
<td>Q1</td>
<td>67.56</td>
<td>40.31</td>
<td>144</td>
<td>-88.25</td>
<td>11.3</td>
</tr>
<tr>
<td>Q2</td>
<td>67.66</td>
<td>40.84</td>
<td>144</td>
<td>-87.41</td>
<td>12.7</td>
</tr>
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<td>40.56</td>
<td>144</td>
<td>-88.11</td>
<td>14.1</td>
</tr>
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<td>Q4</td>
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<td>40.92</td>
<td>144</td>
<td>-87.77</td>
<td>14.1</td>
</tr>
</tbody>
</table>

In the SF$_{5}$ system, the five fluorine atoms are arranged in a square pyramidal geometry. The axial fluorine atom is unique in the system and can be considered the top of the pyramid. The four equatorial fluorine atoms can be considered magnetically equivalent and comprise the base of the pyramid. The axial fluorine atom of the SF$_{5}$ group exhibits a quintet due to the signal split by the other four equatorial fluorine atoms adjacent to the sulfur atom.
The four equatorial fluorine atoms exhibit a doublet of triplets upfield of the axial fluorine atom quintet signal. The difluoromethylene group of each compound can also be observed by $^{19}$F NMR spectroscopy. The two fluorine atoms bonded to the carbon atom couple to the four equatorial fluorine atoms of the vicinal pentafluorosulfanyl group, are observed as a quintet. Coupling between the fluorine atoms of the difluoromethylene group and the axial fluorine atom of the pentafluorosulfanyl group was not large enough to be observed.

The $^1$H NMR and $^{13}$C NMR spectra have been collected for the compounds discussed in this chapter. Due to the spatial arrangement of the pentafluorosulfanyl difluoromethylene group in these compounds, no fluorine to hydrogen atom coupling is observed. Some of the NMR spectra presented have a low signal-to-noise ratio. This is due to the low solubility of the compounds in deuterated acetone and deuterated chloroform at room temperature. The solubility of compounds 6-9, 11, 12, and Q1-Q4 in acetone were higher in heated acetone, allowing for the growth of small crystals. By using deuterated DMSO, the compounds can be dissolved. The quinazolinones being studied in deuterated DMSO began to decompose, causing impurities to appear in the spectra of these compounds.

Further characterization was carried out using IR spectroscopy. There are several regions of each spectrum where absorption bands are shared by each compound as listed in Table 3.2. These bands are present due to common structural features among the compounds. For example, they all share the SF$_5$CF$_2$ functional group. Sulfur-fluorine stretches can be observed in the spectrum of each compound between 780-870 cm$^{-1}$. Sulfur-fluorine deformation can be observed in the spectrum of each compound at approximately 600 cm$^{-1}$. The ranges of these stretches and deformations are located in
the expected regions.\textsuperscript{18} Absorption bands for C-F stretching can be observed around 1100 cm\textsuperscript{-1} as well.\textsuperscript{19} The aromatic primary amides and secondary amides N-H stretch absorptions are observed around 3000 cm\textsuperscript{-1}. The vibrational bands of amide I (C=O stretching) and amide II (NH bending) are listed in Table 3.2.\textsuperscript{20}

Table 3.2. IR bands of compounds 6-8, 11, 12, and Q1-Q3.

<table>
<thead>
<tr>
<th>Compound</th>
<th>S-F absorptions (cm\textsuperscript{-1})</th>
<th>C-F absorptions (cm\textsuperscript{-1})</th>
<th>Amide I absorptions (cm\textsuperscript{-1})</th>
<th>Amide II absorptions (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>826, 781</td>
<td>1155, 1133</td>
<td>1672</td>
<td>1618</td>
</tr>
<tr>
<td>7</td>
<td>848, 823</td>
<td>1159, 1132, 1115</td>
<td>1682</td>
<td>1629-1606</td>
</tr>
<tr>
<td>8</td>
<td>853, 819</td>
<td>1164, 1145, 1115</td>
<td>1670</td>
<td>1621-1591</td>
</tr>
<tr>
<td>11</td>
<td>851, 826</td>
<td>1179, 1154, 1141, 1109</td>
<td>1727</td>
<td>1618-1548</td>
</tr>
<tr>
<td>12</td>
<td>863, 830</td>
<td>1178, 1153, 1136, 1102</td>
<td>1742</td>
<td>1617-1520</td>
</tr>
<tr>
<td>Q1</td>
<td>797, 781</td>
<td>1199, 1155, 1133</td>
<td>1674</td>
<td>1630-1619</td>
</tr>
<tr>
<td>Q2</td>
<td>847, 822</td>
<td>1159, 1131, 1115</td>
<td>1679</td>
<td>1628-1606</td>
</tr>
<tr>
<td>Q3</td>
<td>854, 821</td>
<td>1164, 1115</td>
<td>1670</td>
<td>1623-1591</td>
</tr>
</tbody>
</table>

Besides the spectroscopic characterization of the SF\textsubscript{5}CF\textsubscript{2}-containing compounds, crystals of decent quality for single crystal X-ray diffraction were obtained for compounds Q1-Q5 and 11-12 as shown in Figure 3.2. Both compounds 11 and 12 feature benzofuran moieties with the SF\textsubscript{5}CF\textsubscript{2}C(O)NH\textsuperscript{-} group bonded to the “2” position of the furan ring. The SF\textsubscript{5}CF\textsubscript{2}-containing compounds Q1-Q4 belong to the class of compounds known as 4-(3H)-quinazolinones. Compound Q5 may be considered a pyrimidin-4(3H)-one, due to the
thiophene ring fused to the pyrimidine ring of the compound. Each of the quinazolinones, aside from compound Q5, differ in the substituent bonded to the phenylene ring of each structure. The two nitrogen atoms on the ring of SF$_5$CF$_2$-containing quinazolinones Q1-Q5 have considerably different bond lengths as listed in Table 3.3. From the bond lengths of the two nitrogen atoms (N1) and (N2) to the carbon atom to which they are both bonded, the nitrogen atom which has a bond to a hydrogen atom can be better determined. The shorter N-C bond (~1.28 Å) is more likely to be a double bond, leaving the hydrogen atom to be bonded to the nitrogen atom with the longer C-N bond length (~1.37 Å).\footnote{Error! Reference source not found.}

Table 3.3. C-N bond lengths for compounds Q1-Q5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>N1-C1</td>
<td>1.369(2)</td>
</tr>
<tr>
<td></td>
<td>N2-C1</td>
<td>1.283(2)</td>
</tr>
<tr>
<td>Q2</td>
<td>N1-C1</td>
<td>1.279(3)</td>
</tr>
<tr>
<td></td>
<td>N2-C1</td>
<td>1.369(3)</td>
</tr>
<tr>
<td>Q3</td>
<td>N1-C1</td>
<td>1.283(4)</td>
</tr>
<tr>
<td></td>
<td>N2-C1</td>
<td>1.368(4)</td>
</tr>
<tr>
<td>Q4</td>
<td>N1-C1</td>
<td>1.369(2)</td>
</tr>
<tr>
<td></td>
<td>N2-C1</td>
<td>1.283(2)</td>
</tr>
<tr>
<td>Q5</td>
<td>N1-C6</td>
<td>1.360(4)</td>
</tr>
<tr>
<td></td>
<td>N2-C6</td>
<td>1.285(4)</td>
</tr>
</tbody>
</table>
The geometry and conformation of the fluorine-bearing \( \text{SF}_5\text{CF}_2^- \) group is of great interest.

Figure 3.2. Crystal structures of compound 11-12, and Q1-Q5. Color code: Fluorine-Green, Chlorine-Light green, Blue-Nitrogen, Red-Oxygen, Yellow-Sulfur, Grey-Carbon, and White-Hydrogen.

As listed in Table 3.4, the sulfur (\( \text{SF}_5 \) group)-to-carbon (\( \text{CF}_2 \) group)-to carbon (ring) bond angles are given for compounds Q1-Q5. In each of the structures, the pentafluorosulfanyl moiety is projected out of the plane of the aromatic ring, or thiophene
ring of the given structure. The size of the S-C-C bond angles can be explained by Bent’s rule.\textsuperscript{22} The CF\textsubscript{2}-containing carbon atom is bonded to two fluorine atoms, and the orbitals of each bond should have slightly higher “p-character,” than a covalent bond between two carbon atoms. As a result, there will be greater “s-character,” in the orbitals of the bonds between the CF\textsubscript{2}-carbon and the ring carbon atom, as well as the CF\textsubscript{2}-carbon atom and the SF\textsubscript{5}-sulfur atom. This increase in “s-character,” will widen the bond angles between these atoms.

Table 3.4. S-C-C bond angles for compounds Q1-Q5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Angle of measurement</th>
<th>Angle measurement (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>C1-C10-S1</td>
<td>113.9(3)</td>
</tr>
<tr>
<td>Q2</td>
<td>C1-C9-S1</td>
<td>114.2(2)</td>
</tr>
<tr>
<td>Q3</td>
<td>C1-C10-S1</td>
<td>114.2(2)</td>
</tr>
<tr>
<td>Q4</td>
<td>C2-C1-S1</td>
<td>114.14(10)</td>
</tr>
<tr>
<td>Q5</td>
<td>C6-C7-S2</td>
<td>113.7(2)</td>
</tr>
</tbody>
</table>

Compounds 11 and 12 feature several interesting torsions between the amide functionality and the benzofuran group. The pentafluorosulfanyldifluoromethyl-acetoamide functional group of compound 11 forms a plane which has a dihedral angle of -28° with respect to the plane formed by the benzofuran moiety. This dihedral angle is also observed in compound 12, however it is larger, at -43°. A plausible reason for the larger dihedral angle of compound 12 is repulsion between the nitrile group bonded to carbon atom C1 and the carbonyl oxygen atom O2.
Numerous intermolecular and intramolecular interactions were observed and measured in these crystal structures, and their packing structures are illustrated in the Appendix. In general, the carbonyl oxygen is a very good H-bond acceptor, which is also true in all the crystal structures being discussed in this Chapter as listed in Table 3.5. The H···O bonds are all close to linear, while some of the hydrogen bonds containing fluorine are hardly linear.

Whether F is a H-bond acceptor or not has been debated. When Pauling originally stated that: “It is found empirically that fluorine forms very strong hydrogen bonds, oxygen weaker ones and nitrogen still weaker ones”, he was discussing non-covalently bonded fluorine atoms. Later, the ability of covalently bonded fluorine to act as a hydrogen bond acceptor was doubted by Pauling as well as others. However, several experimental evidences and computational proofs of fluorine as a hydrogen bond acceptor have been reported in recent years. According to the IUPAC recommended definition of the hydrogen bond, “The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.” As stated in the same article: “The X–H···Y angle is usually linear (180°) and the closer the angle is to 180°, the stronger is the hydrogen bond and the shorter is the H···Y distance.” Among the listed hydrogen bonds, H···O bonds are mostly close to 180°; however, several H···F interactions exhibit an angle far from 180°. Therefore, these non-linear H···F contacts might be incidental instead of being an attractive interaction between the hydrogen atom and the fluorine atom of another molecule.
Another type of interaction of interest is the interaction between two fluorine atoms. Depending on the net interactions, halogen atoms can behave as both an electron-rich site and an electron-poor site. The IUPAC definition of a halogen bond states: “A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.” A common situation is that the donor and the acceptor of a halogen bond are different atoms. However, in the crystal structures reported in this work, several F···F short contact distances were measured. These contact distances and associated angles are listed in Table 3.6. The distance can be as short as 2.637 Å, which is much less than the sum of the van der Waal’s radii of two fluorine atoms. As listed in Table 3.6, two types of noncovalent F···F contacts were observed. Halogen bonding is more likely to be observed for molecules containing bromine or iodine due to the larger distance of outer orbital electrons allowing for the presence of a σ-hole.

The concept of the σ-hole as an electron deficient region can be applied to explain halogen bonding. However, fluorine atoms are highly non-polarizable, therefore, observing fluorine-to-fluorine halogen bonding is unlikely. Recently, noncovalent electrostatic interactions in self-assembled hexafluorobenzene (C₆F₆) and hexabromobenzene (C₆Br₆) networks were revealed using itProbe, an AFM-based method, and two-dimensional bonding structures were successfully imaged. The itProbe measurement presented analogous features for both C₆F₆ and C₆Br₆. The type II F···F halogen bond is less common than the type I F···F halogen bond. However, type II geometry is usually observed for the heavier halogen atoms. Type II halogen bonds are considered as an attractive interaction due to the linear directionality of the halogen bond donor and halogen bond acceptor. The nonlinear interactions are most likely to be incidental.
Table 3.5. Hydrogen bonds in the crystal structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>11</strong></td>
<td>O1···H2B-N2 (intra)</td>
<td>2.431</td>
<td>104.37</td>
</tr>
<tr>
<td></td>
<td>O3···H2A-N2</td>
<td>2.100</td>
<td>157.69</td>
</tr>
<tr>
<td></td>
<td>O3···H1-N1 (intra)</td>
<td>2.168</td>
<td>121.90</td>
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<tr>
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<td>F4···H2B-N2</td>
<td>2.461</td>
<td>152.88</td>
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<tr>
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<td>F5···H6-C6</td>
<td>2.641</td>
<td>142.81</td>
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<td><strong>12</strong></td>
<td>F4···H5-C5</td>
<td>2.630</td>
<td>131.79</td>
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<td>O2···H1-N1</td>
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<td>162.31</td>
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<td>O1···H2-N2</td>
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<td>169.34</td>
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<tr>
<td></td>
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<td>140.84</td>
</tr>
<tr>
<td><strong>Q2</strong></td>
<td>F2···H5-C5</td>
<td>2.734</td>
<td>123.3</td>
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<td></td>
<td>F4···H8-C8</td>
<td>2.956</td>
<td>166.77</td>
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<td>O1···H2-N2</td>
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<td>168.52</td>
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<td>2.824</td>
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<td>118.8</td>
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<td>111.3</td>
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<tr>
<td><strong>Q3</strong></td>
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</tr>
<tr>
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<td>2.625</td>
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<td></td>
<td>F5···H9B-C9</td>
<td>2.571</td>
<td>118.80</td>
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<td>F2···H2-N2 (intra)</td>
<td>2.384</td>
<td>101.94</td>
</tr>
<tr>
<td><strong>Q4</strong></td>
<td>O1···H1-N1</td>
<td>1.926</td>
<td>168.04</td>
</tr>
<tr>
<td></td>
<td>F3···H9-C9</td>
<td>2.593</td>
<td>165.04</td>
</tr>
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<td>F1···H1-N1 (intra)</td>
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<td>100.99</td>
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<td>F7···H2-C2</td>
<td>2.338</td>
<td>143.14</td>
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</table>
Given the lack of linearity in the interactions presented in Table 3.6, it is most likely that the fluorine-to-fluorine contacts observed in compounds 11, 12, and Q1-Q5 are incidental. A further study involving the use of an o-aminobenzamide starting material that contains a bromine or iodine atom may provide a quinazolinone that possesses a halogen bonding interaction.

Table 3.6. F···F short distance contacts and interaction angles.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Contact</th>
<th>Interaction length (Å)</th>
<th>Interaction angle (°)</th>
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<tbody>
<tr>
<td>11</td>
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<td>2.918</td>
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<td></td>
<td>S1-F7···F3 = 113.76(7)</td>
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<tr>
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<td>F2···F3</td>
<td>2.846</td>
<td>C11-F2···F3 = 109.1(2)</td>
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<td></td>
<td>S1-F3···F2 = 113.7(1)</td>
</tr>
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<td>F3···F7</td>
<td>2.933</td>
<td>S1-F7···F3 = 159.8(1)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>S1-F3···F7 = 109.2(1)</td>
</tr>
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<td>F4···F5</td>
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<td>S1-F4···F5 = 160.5(1)</td>
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<td>S1-F5···F4 = 108.2(1)</td>
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<td></td>
<td>S1-F7···F4 = 114.8(1)</td>
</tr>
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<td>F6···F7</td>
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<td>S1-F6···F7 = 114.3(2)</td>
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<td>S1-F7···F6 = 136.6(2)</td>
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<td>F2···F4</td>
<td>2.739</td>
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<td>F7···F6</td>
<td>2.778</td>
<td>S1-F6···F7 = 114.0(2)</td>
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<td>C1-F2···F3 = 150.33(9)</td>
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<td>F3···F5</td>
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<td>S2-F3···F5 = 142.0(1)</td>
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<td>2.931</td>
<td>S2-F3···F3 = 102.0(1)</td>
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<td>F1···F6</td>
<td>2.788</td>
<td>C7-F1···F6 = 151.5(2)</td>
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<td>S2-F6···F1 = 137.1(2)</td>
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</table>
3.4 Conclusions

A variety of SF$_5$CF$_2$-substituted 4-quinazolinones have been successfully synthesized and characterized. The synthesis of SF$_5$CF$_2$-containing quinazolinones has only been achieved through an acid catalyzed cyclization of α-amido pentafluorosulfanyldifluoroacetoamides. A base catalyzed cyclization could be attempted in the future. The reaction of pentafluorosulfanyldifluoro acetyl chloride with 3-benzofuran-2-carboxamide produces different products depending on the base used in the reaction. It is not known if this behavior can be observed in reactions involving other o-amino benzamides with pentafluorosulfanyldifluoro acetyl chloride. Using $^{19}$F NMR analysis, the chemical shifts of the peaks for each compound show minor changes despite the differences in each structure. In the crystal structures of the SF$_5$CF$_2$-containing products, hydrogen bonds involving in fluorine atoms were observed.

3.5 References


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CHAPTER FOUR

SYNTHESIS AND CHARACTERIZATION OF SF5CF2H

4.1 Introduction

Short chain perfluoroalkanes containing a primary pentafluorosulfanyl group were initially synthesized in the early 1950s.¹ A few of the compounds synthesized include pentafluorosulfanyl-trifluoromethane, 1-pentafluorosulfanyl-pentafluoroethane, 1-pentafluorosulfanyl heptafluoropropane, and 1-pentafluorosulfanyl nonafluoro-n-butane. These compounds, such as pentafluorosulfanyl trifluoromethane, pentafluorosulfanyl pentafluoroethane have been proposed for several applications, including as fire retardants and refrigerant fluids.² A disadvantage to using SF5CF3 for these applications is the high GWP (global warming potential) of the compound, which is 19,000, relative to CO2.³ This is due to the compound’s high absorption of IR wavelengths between 800 cm⁻¹ and 1200 cm⁻¹. Additionally, the long atmospheric lifetime of SF5CF3, estimated to be between a few hundred and a few thousand years also contributes to its high global warming potential (GWP).

A proposed substitute for SF5CF3 is SF5CF2H, pentafluorosulfanyl difluoromethane. Several patents have been filed which demonstrate the use of SF5CF2H as a foam blowing agent, and as a refrigerant.²,⁴ One issue with the widespread use of SF5CF2H as a refrigerant would likely be its GWP, which may be large. A blended refrigerant, where small amounts of SF5CF2H are used, may provide an option to formulate an efficient refrigerant which can minimize the greenhouse effect created by inclusion of SF5CF2H. In 1950, the first synthesis of pentafluorosulfanyl trifluoromethane was reported by Cady.⁵ The compound was formed by the reaction of methanethiol with cobalt trifluoride, an example of oxidative fluorination. Of note, pentafluorosulfanyl
difluoromethane was also formed in the oxidative fluorination of methanethiol by cobalt trifluoride. The yield was quite low, 15%. Unfortunately, the characterization of the compound was limited to elemental analysis, and a boiling point determination. The elemental analysis showed that the material had an empirical formula of CHSF₇. The boiling point was determined to be approximately 5 °C. Although most scientists in the field of fluorine chemistry have since felt that this compound was indeed SF₅CF₂H, no viable alternative syntheses have yet been reported for this compound.

Herein, an improved synthesis of SF₅CF₂H, based on the reduction of SF₅CF₂I by either tri-n-butyl tin hydride or triethylborane dissolved in hexanes, is reported. Tri-n-butyl tin hydride is commonly used as a reducing agent, and it can be used to reduce fluoroalkyl iodides to fluoroalkanes. Triethylborane has also been used to reduce SF₅CF₂CF₂I to SF₅CF₂CF₂H. Additionally, spectroscopic characterization of SF₅CF₂H is reported for the first time. This characterization includes NMR spectroscopy, IR spectroscopy, and Raman spectroscopy. A mass spectrum of SF₅CF₂H is also presented.

4.2 Experimental

Reactions were performed using flame dried glassware. Reagents were added to glassware either by vacuum-line transfer or were transferred via syringe through a rubber septum. Tri-n-butyl tin hydride was purchased from Sigma-Aldrich and used without purification. Difluoriodopentafluorosulfanylmethane was prepared by literature methods. Anhydrous solvents (toluene) were obtained by distillation over sodium, and subsequent storage on 3 Å molecular sieves.

IR spectroscopy was recorded using a Nicolet IS5 spectrometer. The ¹H NMR (300 MHz), ¹⁹F NMR (283 MHz), and ¹³C NMR (75.5 MHz) spectra were recorded with a JEOL ECX-300 NMR spectrometer. An IR spectrum was recorded using a Thermo Fisher
Scientific Nicolet iS5 spectrometer. The sample was in the gas phase and held at room temperature. A Raman spectrum was collected on a custom instrument in the laboratory of Prof. George Chumanov. The incident beam was produced by a 514.5 nm laser, with a power rating of 0.5 W. The Raman sample was held in a quartz tube, and the analysis done at room temperature. Chemical shifts are expressed in terms of ppm. Internal standards used were C$_6$D$_6$, and CCl$_3$F. The reference values for these solvents are as follows: Benzene-d$_6$= 7.16 ppm ($^1$H), trichlorofluoromethane= 0.00 ppm ($^{19}$F). Mass spectral analysis was performed using a Shimadzu coupled gas chromatograph and mass spectral instrument.

4.2.1 Procedures for the synthesis of SF$_5$CF$_2$H

(A) A three-necked, 100-mL round-bottomed flask, fitted with a stir bar, a rubber septum on one neck, a glass stopper on another neck, and a Kontes® valve adaptor on the center neck, was evacuated and flame dried. Next, 1.0 mmol (0.30 g) of SF$_5$CF$_2$I was condensed into the flask by vacuum-line transfer. The flask was then chilled to -78 °C by immersion in a dry ice filled Dewar. The flask was then connected to a stream of dry nitrogen gas for several minutes. Once the nitrogen had purged the flask for several minutes, the connection to the nitrogen was removed. The flask was then filled with 10 mL of anhydrous toluene and stirring was commenced. Next, 1.3 mmol, 0.33 mL of tri-$n$-butyl tin hydride was injected into the flask using a syringe. This was done slowly, over the course of several hours so as to disperse or spread out the entering reagent. The needle of the syringe was also pressed to the wall of the flask while the tri-$n$-butyl tin hydride was being added. The reaction was stirred overnight while being held at -78 °C. Once the reaction had stirred overnight, the contents of the flask were distilled by trap-to-trap distillation, using a vacuum line. Several "U" traps were connected to the 100-mL flask in series, and the volatile mixture was passed through these traps.
The first trap was held at -95 °C. In this trap, SF₅CF₂I, toluene, and any tributyltin hydride were stopped. The next trap was held at -126 °C, and this trap stopped most of the SF₅CF₂H produced. The final trap was held at -196 °C, and any side products, which may have been formed in the reaction such as CH₂F₂, were held in this trap. Some of the SF₅CF₂H may pass to the -196 °C trap, making a subsequent distillation sometimes necessary. From this reaction, 0.38 mmol, 0.068 g of SF₅CF₂H was recovered, giving a 38% yield.

(B) A two-necked, 250-mL round-bottomed flask, fitted with a stir bar, a rubber septum on one neck, and a Kontes® valve adaptor on the other neck was flame dried on a vacuum line. Next, 1.0 mmol, 0.30 g of SF₅CF₂I was condensed into the flask by vacuum line transfer. The flask was chilled to -78 °C, and a stream of dry nitrogen gas was passed through the flask for several minutes. Once the purging of the flask with nitrogen was complete, 1.1 mL of a 1 M triethylborane in hexanes solution was dripped into the flask over the course of 15 minutes. After the addition, the flask was re-evacuated on the vacuum line, while keeping the flask chilled to -196 °C. Next, the flask was warmed slowly to -50 °C, and the contents of the flask were stirred for three hours at this temperature. After stirring for three hours at -50 °C, the contents of the flask were slowly warmed to room temperature, while maintaining stirring on the reaction mixture. The stirring of the reaction mixture proceeded for 21 hours. After the stirring period, the contents of the flask were distilled by trap-to-trap distillation. Two traps were used. One trap was held at -110 °C, and the second trap was kept at -196 °C. The product was trapped primarily in the -196 °C trap. The yield of the product was 0.087 g, 0.49 mmol. The percent yield of the product was 49%.
To prepare an NMR sample, 0.2 mmol of SF$_5$CF$_2$H was condensed into a Young's tube, along with 1 mL of C$_6$D$_6$. To prepare a gas phase IR sample, a pressure of 10 Torr of SF$_5$CF$_2$H was expanded into a borosilicate glass IR cell, equipped with silicon windows. 

$^1$H NMR (300 Hz, C$_6$D$_6$) δ 4.89 (m, 1H, J = 56 Hz). $^{19}$F NMR (282 Hz, C$_6$D$_6$, 20 °C) δ 67.61 (m, 1F, J= 147 Hz), 36.55 (d, 4 F, J= 147 Hz), -103.27 (d, 2F, J= 56 Hz). 

$^{13}$C NMR (125 MHz, C$_6$D$_6$) δ 119.2 (tq, $^2$J = 176 Hz, $^3$J = 19 Hz). IR: 3020 (vw), 1361 (w), 1328 (w), 1174 (vs), 921 (s), 886 (vs), 741 (s), 676 (w), 621 (m), 615 (m), 584 (m) cm$^{-1}$. 

Raman: 3020 (w), 2966 (w), 2948 (w), 2923 (w), 2889 (w), 2880 (w), 2865 (w), 1169 (w), 1152 (m), 885 (w), 741 (s), 677 (vs), 615 (w), 584 (w), 490 (w), 483 (w), 345 (m), 317 (w) cm$^{-1}$. 

4.2.2 *Synthesis of p-pentafluoroethylanisole*

To a 100 mL, three-necked round-bottomed flask, equipped with a stir bar and a rubber septum, 0.099 g, 0.001 mol of copper (I) chloride and 0.22 g, 0.0020 mol of potassium tert-butoxide were added in a dry box. The flask was fitted with a Kontes® valve adaptor, and 10 mL of anhydrous DMF was injected into the flask. Next, 0.18 g, 0.0010 mol of CF$_3$CF$_2$H was condensed into the flask. The flask was slowly warmed to room temperature, and the contents of the flask were stirred for 30 minutes. At this time 0.23 g, 0.001 mol of 4-iodoanisole was dissolved in 5 ml of anhydrous DMF, and the solution subsequently injected into the reaction flask. The flask was then heated to 70 °C. An aliquots of the reaction solution was injected into a NMR tube after 2 hours of heating. No evidence of a pentafluorosulfanyldifluoromethane transfer reaction by $^{19}$F NMR spectroscopy could be observed.
4.2.3 **Attempted preparation of p-pentafluorosulfanyl anisole**

To a 100 mL, three-necked round-bottomed flask, equipped with a stir bar and a rubber septum, 0.099 g, 0.001 mol of copper (I) chloride and 0.22 g, 0.0020 mol of potassium tert-butoxide were added in a dry box. The flask was fitted with a Kontes® valve adaptor, and 10 mL of anhydrous DMF was injected into the flask. Next, 0.18 g, 0.0011 mol of SF$_5$CF$_2$H was condensed into the flask. The flask was slowly warmed to room temperature, and the contents of the flask were stirred for 30 minutes. At this time 0.23 g, 0.001 mol of 4-iodoanisole was dissolved in 5 ml of anhydrous DMF, and the solution subsequently injected into the reaction flask. The flask was then heated to 70 °C. An aliquots of the reaction solution was injected into a NMR tube after 2 hours of heating. No evidence of a pentafluorosulfanyldifluoromethane transfer reaction by $^{19}$F NMR spectroscopy could be observed.

4.2.4 **Attempted preparation of pentafluorosulfanyltrimethylsilane**

To a 100 mL, three-necked round-bottomed flask, equipped with a stir bar, Kontes® valve adaptor, and a rubber septum, 1 mL of a 1 M potassium bis(trimethylsilyl)amide solution was injected. Next, 10 mL of anhydrous toluene was injected into the flask. At this time, 0.18 g 0.001 mol of SF$_5$CF$_2$H, and 0.11 g, 0.001 mol of chlorotrimethylsilane were condensed into the flask. The flask was slowly warmed to room temperature, and the contents of the flask were stirred for 12 hours. At this time, an aliquot of the reaction solution was injected into a NMR tube. By $^{19}$F NMR spectroscopy, only the existence of 4-fluorotoluene could be observed.
4.3 Results and Discussion

Pentafluorosulfanyl difluoromethane has been prepared using two new synthetic routes, shown in Scheme 4.1. In both cases, SF₅CF₂I is mixed with a reducing agent. Firstly, by mixing SF₅CF₂I with tri-n-butyl tin hydride at low temperature, SF₅CF₂H can be produced in a 37% yield. This was achieved by slowly running tri-n-butyl tin hydride down the side of the reaction flask’s wall into a solution of SF₅CF₂I in toluene, held at -78 °C. When the reaction is attempted at room temperature, SF₄, difluoromethane, and HF are the only observable products. Decomposition of SF₅CF₂I into SF₄, HF, and difluoromethane may account for some of the yield loss in the low temperature reaction of tri-n-butyl tin hydride with SF₅CF₂I. Second, by mixing SF₅CF₂I with a 1.0 M solution of triethylborane in hexanes, SF₅CF₂H can be recovered in a 49% yield. The triethylborane reaction solution was held at -50 °C for several hours before the reaction mixture was warmed to room temperature. This was done to prevent decomposition products from forming during the reaction. It is unknown as to whether SF₅CF₂I will decompose when mixed with triethylborane at a higher temperature. No attempts were made to mix SF₅CF₂I with hexanes in the absence of triethylborane. The hydro compound SF₅CF₂H is stable at room temperature and can be stored in a 316-stainless steel cylinder for an extended time without decomposition.

Several chemical reactions involving SF₅CF₂H were attempted. First, SF₅CF₂H was mixed with KHMDs and chlorotrimethylsilane, in toluene, to generate pentafluorosulfanyldifluoromethyl trimethylsilane, shown in Scheme 4.2. This reaction is similar to the reaction of CF₃H with ClSi(Me)₃, using KHMDs as a base. The only product recovered from this reaction was p-fluorotoluene, as observed by ¹⁹F NMR spectroscopy.
A second reaction was conducted with SF$_5$CF$_2$H, in a manner analogous to the copper-mediated trifluoromethylation and pentafluoroethylation reactions discovered by Grushin and co-workers, shown in 

**Scheme 4.3.**

Scheme 4.1. Syntheses of SF$_5$CF$_2$H by reductive methods.

![Scheme 4.1](image)

**Scheme 4.2.** Attempted preparation of SF$_5$CF$_2$Si(CH$_3$)$_3$.

![Scheme 4.2](image)

To a [K(DMF)$_2$][t-BuO$_2$Cu] complex, SF$_5$CF$_2$H and 4-iodoanisole were added. The reaction did not proceed, and SF$_5$CF$_2$H was recovered. It is unknown as to the reason why SF$_5$CF$_2$H does not react with the complex. An analogous experiment with CF$_3$CF$_2$H
and 4-iodoanisole was performed. The product, 4-pentafluoroethylanisole, was recovered in 84% yield.

When comparing the synthesis of SF₅CF₂H to those of SF₅CF₃, SF₅CH₂F, and SF₅CF₃, several differences can be observed. Both SF₅CF₂H and SF₅CF₃ were generated by an oxidative fluorination mechanism.⁵

![Scheme 4.3. Attempted preparation of 1-pentafluorosulfanyldifluoromethyl-4-methoxybenzene.](image)

Interestingly, SF₅CH₃ can be generated by a reduction as shown in Scheme 4.4, which is similar to the path used to synthesize SF₅CF₂H shown here.¹¹ First, SF₅Cl was added to ketene. The resulting SF₅CH₂C(O)Cl was hydrolyzed to SF₅CH₂C(O)OH, and a silver salt was formed from the acid. The silver salt can be heated in the presence of bromine to eliminate a CO₂ group from the molecule, and form SF₅CH₂Br. From here, SF₅CH₂Br can be reduced by zinc metal dissolved in HCl, to generate SF₅CH₃.

A similar technique can be used to synthesize SF₅CF₂I, as covered in Chapter 1.¹² The synthesis of SF₅CH₂F is slightly different from SF₅CH₃ and SF₅CF₂H as shown in Scheme 4.5, in that the reaction is an oxidative fluorination.¹³ First, the compound mercuric bis(trifluoromethylamide) is formed by the action of HgF₂ on CF₃N=CF₂. From
mercuric bis(trifluoromethylamide), a reaction will occur at room temperature with methanesulfonyl chloride to generate bis-trifluoromethylamino-sulfur methane.

\[
\begin{align*}
\text{F}_5\text{S} &= \text{CH}_2\text{Br} \quad + \quad \text{Zn/HCl} & \quad \rightarrow \quad \text{F}_5\text{S} &= \text{CH}_3
\end{align*}
\]

Scheme 4.4. The synthesis of SF$_5$CH$_3$.

By oxidative fluorination of bis-trifluoromethyl aminosulfur methane over AgF$_2$, pentafluorosulfanylfluoromethane can be synthesized in an 86% yield. Of the syntheses of the pentafluorosulfanyl-containing methanes and fluoromethanes, three have been synthesized by oxidative fluorinations, SF$_5$CF$_3$, SF$_5$CF$_2$H, and SF$_5$CH$_2$F, and two by reductions, SF$_5$CH$_3$ and SF$_5$CF$_2$H. Only SF$_5$CF$_2$H has been synthesized by both oxidative fluorination as well as reduction.

From the $^{19}$F NMR spectrum of SF$_5$CF$_2$H, peaks for the fluorine atoms attached to the sulfur, as well as fluorine atoms attached to the carbon can be observed, as shown in Figure 4.1. The chemical shifts as well as the coupling constants from the $^{19}$F NMR spectra of SF$_5$CF$_3$, SF$_5$CF$_2$H, and SF$_5$CFH$_2$ are presented in Table 4.1.

The coupling constant for the axial fluorine atom to the fluorine atoms bonded to the carbon was observed in the case of SF$_5$CF$_3$. For both SF$_5$CH$_2$F and SF$_5$CF$_2$H, this
coupling was not observed. Table 4.1. $^{19}$F NMR signals for SF$_5$CF$_2$H, SF$_5$CF$_3$, SF$_5$CH$_2$F, SF$_5$CF$_2$H. The fluorine atoms on the sulfur are represented by an AB$_2$X$_2$ pattern. The signal for the axial fluorine atom bonded to sulfur in SF$_5$CF$_2$H is observed as a quintet at 67.61 ppm.

![Scheme 4.5. The synthesis of SF$_5$CH$_2$F.](image)

No additional coupling from the axial fluorine atom bonded to sulfur to the fluorine or hydrogen atoms bonded to carbon can be observed. Fluorine coupling from the axial fluorine atom of the pentafluorosulfanyl group to the fluorine atoms bonded to the carbon adjacent to the sulfur atom was not observed for SF$_5$CFH$_2$. This may be due to an inability to observe the coupling with the NMR spectrometers used for each experiment. The equatorial fluorine atoms bonded to sulfur in SF$_5$CF$_2$H are represented by a doublet of triplets at 36.28 ppm. The coupling constant for the axial fluorine atom bonded to sulfur to the equatorial fluorine atoms bonded to sulfur is 147 Hz. The signal corresponding to the fluorine atom bonded to carbon in SF$_5$CF$_2$H appears as a doublet of quintets, at -103.27 Hz as shown in Figure 4.1. The coupling constant for the proton to fluorine atom bonded to carbon is 56 Hz. The chemical shifts of the fluorine atoms in SF$_5$CF$_2$H, as well
as the coupling constants appear to be within a reasonable range of SF₅CF₂CF₂H.¹⁴ The ¹⁹F NMR spectra data of SF₅CF₃, and SF₅CH₂F can be compared to the data for SF₅CF₂H as shown in Figure 4.1.

From the ¹H NMR spectrum of SF₅CF₂H, a triplet of quintets can be observed at 4.89 ppm as shown in Figure 4.2. The proton-to-equatorial sulfur fluorine coupling for this signal is 6 Hz, and the coupling constant between the fluorine atoms bonded to carbon and the hydrogen atom is 54 Hz. There is a slight difference of this measured value of 2 Hz from the constant measured by ¹⁹F NMR spectroscopy. Coupling of the hydrogen atom to fluorine atoms bonded to the carbon atom, as well as the four equatorial fluorine atoms bonded to sulfur is observed. The chemical shift and coupling data from the ¹H NMR spectra of SF₅CF₂H, SF₅CH₂F, and SF₅CH₃ are listed in Table 4.¹¹b, ¹³

In the ¹³C NMR spectrum of SF₅CF₂H, shown in

Figure 4.3, a triplet of quintets for the carbon atom in SF₅CF₂H is observed, due to coupling from the fluorine atoms bonded to carbon, as well as the equatorial fluorine atoms
bonded to sulfur. The chemical shift of this peak is observed at 119.2 ppm. The coupling constant of the equatorial sulfur fluorine atoms to the carbon atom is 32.5 Hz, and the coupling constant of the fluorine atoms bonded to carbon is 296.3 Hz.

In addition to NMR spectroscopy, IR and Raman spectroscopy have also been used to characterize SF$_5$CF$_2$H as shown in Figure 4.4. The IR and Raman spectroscopic data is compared to calculated frequencies and intensity of the vibrational modes of SF$_5$CF$_2$H, presented in

**Table 4.3**

Table 4.3. These calculations were performed using the density functional method PBE0-D3/def2-TZVP.
Table 4.1. $^{19}$F NMR signals for SF$_5$CF$_2$H, SF$_5$CF$_3$, SF$_5$CH$_2$F, SF$_5$CH$_3$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Axial Sulfur-Fluorine Chemical Shift (PPM)</th>
<th>Equatorial Sulfur-Fluorine Chemical Shift (PPM)</th>
<th>$^2$J$<em>{F-F}$ and $^3$J$</em>{F-F}$ Coupling (Hz)</th>
<th>Carbon-Fluorine Chemical Shift (PPM)</th>
<th>$^2$J$<em>{F-H}$ and $^3$J$</em>{F-H}$ Coupling (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_5$CH$_2$F</td>
<td>71.8 (p)</td>
<td>48.2 (ddt)</td>
<td>145.6 (SF$<em>{ax}$-SF$</em>{eq}$) 10.6 (SF$_{eq}$-CF)</td>
<td>-192 (tp)</td>
<td>7.0 (SF$_{eq}$-CH) 45.9 (CF-CH)</td>
</tr>
<tr>
<td>SF$_5$CF$_2$H</td>
<td>67.61 (p)</td>
<td>36.28 (dt)</td>
<td>147 (SF$<em>{ax}$-SF$</em>{eq}$) 11.3 (SF$_{eq}$-CF)</td>
<td>-103.3 (dp)</td>
<td>56.6 (CF-CH) 8.5 (SF$_{eq}$-CF)</td>
</tr>
<tr>
<td>SF$_5$CF$_3$</td>
<td>61.3 (pq)</td>
<td>37.0 (dq)</td>
<td>146 (SF$<em>{ax}$-SF$</em>{eq}$) 21.8 (CF-SF$<em>{eq}$) 6.2 (CF-SF$</em>{ax}$)</td>
<td>-66.2 (p)</td>
<td>N/A</td>
</tr>
<tr>
<td>SF$_5$CH$_3$</td>
<td>84 (q)</td>
<td>71 (d)</td>
<td>150</td>
<td>N/A</td>
<td>10.2 ($^3$J$_{H-F}$)</td>
</tr>
</tbody>
</table>
Figure 4.2. $^1$H NMR spectrum of SF$_5$CF$_2$H.

Table 4.2. $^1$H NMR spectroscopic data for SF$_5$CH$_3$, SF$_5$CH$_2$F, SF$_5$CF$_2$H

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift (PPM)</th>
<th>$^2$J$<em>{H,F}$ and $^3$J$</em>{H,F}$ Coupling (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_5$CH$_3$</td>
<td>3.4 (q)</td>
<td>9.75 (CH-SF$_{eq}$)</td>
</tr>
<tr>
<td>SF$_5$CH$_2$F</td>
<td>4.78 (dq)</td>
<td>7.0 (CH-SF$_{eq}$), 45.9 (CH-CF)</td>
</tr>
<tr>
<td>SF$_5$CF$_2$H</td>
<td>4.89 (tq)</td>
<td>6 (CH-SF$_{eq}$), 54 (CH-CF)</td>
</tr>
</tbody>
</table>

Using simulation data as a guide, SF$_5$CF$_2$H adopts Cs symmetry, with a mirror plane that runs through the carbon atom, sulfur atom, hydrogen atom, and the axial sulfur fluorine atom. A second possible geometry of the molecule would also include two of the equatorial fluorine atoms in the mirror plane of the molecule. In terms of the vibrational bands observed, two possible representations exist. The representation of the vibrational modes is $\Gamma_{vib} = 14 A^\prime + 10 A''$, if the mirror plane which bifurcates the molecule passes
through the sulfur atom, the carbon atom, the hydrogen atom, and the axial sulfur fluorine atom.

Figure 4.3. $^{13}$C NMR spectrum of SF$_5$CF$_2$H.

If the molecule’s structure includes the axial sulfur fluorine atom, two of the equatorial fluorine atoms, the carbon atom, the sulfur atom, and the hydrogen atom in the mirror plane, the representation of the vibrational modes will be $\Gamma_{\text{vib}} = 15 A' + 9 A''$ This determination was first made based on the generation of a reducible representation for the possible symmetry operations which can be applied to SF$_5$CF$_2$H. Reducible representations for the two conformations of SF$_5$CF$_2$H were generated. From these reducible representations, the total number of irreducible representations for each structure were calculated by simple inspection. The translational and rotational modes were subtracted from the total number of irreducible representations to give the vibrational modes for each conformation of SF$_5$CF$_2$H that could have Cs symmetry. The compound
will have 24 vibrationally active modes. This determination is made by calculating the
degrees of freedom that constitute the vibrational modes of SF$_5$CF$_2$H with the formula $3N-6$.$^{15}$ All 24 bands should be observed in the IR spectrum as well as the Raman spectrum
of the compound. However, all the calculated bands are not observed, for both the IR
spectrum and the Raman spectrum. The cause of this is not clear, however, some of the
bands may overlap, making them difficult to be observed. The bands may also fall out of
the range of either the IR or Raman instrument, or are too weak to be detected. The
symmetries of the bands have been assigned based on assignments of SF$_5$Cl and
SF$_5$CF$_3$, as well as CF$_3$CF$_2$H.$^{16}$

Originally, the assignments of IR and Raman vibrational modes for SF$_5$CF$_3$ were
based on characterizing the compound as having $C_{4v}$ symmetry, due to the low barrier of
rotation of the sulfur-to-carbon bond.$^{17}$ These analyses have been adapted to SF$_5$CF$_2$H,
however, due to the lower symmetry of SF$_5$CF$_2$H, $C_s$ symmetry has been applied to the
analysis. Of the vibrational modes observed, several bands overlap, at 3020, 885, 741,
676, 615, and 584 cm$^{-1}$. The band at 3020 cm$^{-1}$ is likely related to the C-H stretch in
SF$_5$CF$_2$H, and can be considered a fundamental band, with $A'$ symmetry. The Raman
bands for SF$_5$CF$_2$H between 2966 and 2865 cm$^{-1}$ are overtones, and their symmetry
cannot be characterized at this time. Furthermore, the carbon-fluorine stretching modes
are observed at 1152, 1174 and 1328 cm$^{-1}$ for SF$_5$CF$_2$H. This provides a close agreement
with the carbon-fluorine stretching frequencies observed for SF$_5$CF$_3$, at 1155, 1174, and
1175 cm$^{-1}$. However, the assignment of symmetry to these peaks is not complete. The
sulfur-to-fluorine stretching modes are observed at 931, 886, 885, and 676 cm$^{-1}$ for
SF$_5$CF$_2$H. The symmetries of the bands have been assigned based on assignments of
SF$_5$Cl, and SF$_5$CF$_3$. The stretching modes of sulfur to fluorine for SF$_5$CF$_3$ are observed at
906, 905, 889, 885, and 685 cm\(^{-1}\), which provides a close match between the two compounds.

Figure 4.4. IR and Raman spectra of SF\(_5\)CF\(_2\)H (The IR spectrum is highlighted in orange; the Raman spectrum is highlighted in purple).

Based on the assignment of stretches in SF\(_5\)CF\(_3\), the signal at 885 cm\(^{-1}\) has been assigned a symmetry of A\(^{\prime}\). The F-C-F bending mode of SF\(_5\)CF\(_3\) is observed at 755 cm\(^{-1}\), and there is correlation with the strong band observed at 741 cm\(^{-1}\) in the IR spectrum of SF\(_5\)CF\(_2\)H. The band at 615 cm\(^{-1}\) in the IR spectrum of SF\(_5\)CF\(_2\)H can be assigned as an F-S-F bend; the IR spectrum of SF\(_5\)CF\(_3\) features a band related to the F-S-F bending mode at 613 cm\(^{-1}\). The band at 584 cm\(^{-1}\) can be characterized as a sulfur to fluorine wagging mode. The characterization of the symmetry of this mode for SF\(_5\)CF\(_3\) was made with the
consideration that SF$_5$CF$_3$ can be considered to have $C_{4v}$ symmetry and has been assigned a symmetry of $e$. This cannot be directly correlated to this mode in SF$_5$CF$_2$H. A band in the spectrum of CF$_3$CF$_2$H, characterized as a wagging mode, has been assigned a symmetry of $A'$. This character assignment is retained for SF$_5$CF$_2$H. The sulfur to carbon stretching mode for SF$_5$CF$_2$H is observed at 317 cm$^{-1}$ in the Raman spectrum. This mode has been assigned a symmetry of $A'$

A GC/MS analysis of SF$_5$CF$_2$H was also carried out, and the fragments are listed in Table 4.4 and shown in Figure 4.5. A parent ion of low intensity was identified at 178 m/z. This ion may also correlate to the SF$_5$CF$_2$ ion, where carbon has a mass of 13 Da. Several fragments have been identified as well.$^{18}$ The fragment with the greatest concentration in the spectrum is observed at 127, belonging to the SF$_5$ ion. This signal may also be caused by iodine impurities in the sample. A second fragment at 177 is also observed, related to the SF$_5$CF$_2$ ion. Several other fragments caused by the decay of the SF$_5$ group can be observed. These fragments are observed at 158, 146, 129, 108, 91, 89, 70, and 51. The fragments related to each peak are SF$_5$=CF$^+$, SF$_6$+, $^{34}$SF$_5$+, SF$_4$+, $^{34}$SF$_3$+, SF$_3$+, SF$_2$+, and SF+, respectively. The peak at 158 may also be caused by a rearrangement of SF$_5$=CF to SF$_4$=CF$_2$. The peaks at 129 and 91 are caused by the $^{34}$S isotope. A significant portion of the peak at 129 has been produced by an unknown analyte. A significant peak at 50 is likely caused by the CF$_2$ fragment. A fragment is observed at 69, related to the CF$_3$ group. The full mass spectrum is shown in the appendix (Figure A.71)
Table 4.3. IR, Raman, and Calculated spectral data for SF<sub>6</sub>CF<sub>2</sub>H. Relative strength guide:
(vs) = very strong, (s) = strong, (m) = medium, (w) = weak, (vw) = very weak.

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4.4 Conclusions

Using SF$_5$CF$_2$I, as well as two reducing agents, SF$_5$CF$_2$H has been synthesized in a higher yield than previously recorded. The highest yield was produced by mixing SF$_5$CF$_2$I with triethylborane in hexanes. The compound SF$_5$CF$_2$H has been characterized by NMR, IR, and Raman spectroscopy. These studies have helped to confirm the synthesis of SF$_5$CF$_2$H. Further techniques that may be used to characterize SF$_5$CF$_2$H include elemental analysis, and gas electron diffraction. Studies of the physical properties of SF$_5$CF$_2$H, such as a confirmation of its boiling point and melting point, as well as generating a vapor pressure curve for the compound should also be carried out in the future. Several reactions were attempted with SF$_5$CF$_2$H to prepare a SF$_5$CF$_2$-transfer
reagent that is analogous to a trifluoromethylating reagent. In these attempts, either no reaction was observed, or the SF₅- group decomposed during the reaction. Further studies into the chemistry of SF₅CF₂H may reveal its utility as a chemical reagent.

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Table A.1. Sample and crystal data for \( N \)-pentafluorosulfanyl-1,3-benzothiazol-2-imine (Compound 1).

<table>
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<tr>
<th>Identification code</th>
<th>( N )-pentafluorosulfanyl-1,3-benzothiazol-2-imine</th>
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<tr>
<td>Empirical formula</td>
<td>( \text{C}_7\text{H}_5\text{F}_5\text{N}_2\text{S}_2 )</td>
</tr>
<tr>
<td>Formula weight</td>
<td>276.25</td>
</tr>
<tr>
<td>Temperature</td>
<td>200(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>( \text{P2}_1/\text{c} )</td>
</tr>
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<td>Unit cell dimensions</td>
<td>( a = 7.3219(15) ) Å</td>
</tr>
<tr>
<td></td>
<td>( b = 14.462(3) ) Å</td>
</tr>
<tr>
<td></td>
<td>( c = 9.1241(18) ) Å</td>
</tr>
<tr>
<td></td>
<td>( \beta = 99.66^\circ(3) )</td>
</tr>
<tr>
<td>Volume</td>
<td>952.4(3) Å(^3)</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.927 Mg/m(^3)</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.607 mm(^{-1})</td>
</tr>
<tr>
<td>( F(000) )</td>
<td>552</td>
</tr>
<tr>
<td>Crystal size</td>
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<tr>
<td>Theta range for data collection</td>
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</tr>
<tr>
<td>Limiting indices</td>
<td>(-8 \leq h \leq 8, -17 \leq k \leq 17, -10 \leq l \leq 10)</td>
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<td>Reflections collected / unique</td>
<td>7660 / 1719 [( R_{\text{int}} = 0.0799 )]</td>
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<tr>
<td>Completeness to theta = 25.24</td>
<td>99.90%</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9588 and 0.7199</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on ( F^2 )</td>
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<td>Data / restraints / parameters</td>
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<td>Goodness-of-fit on ( F^2 )</td>
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<td>Final R indices [( \text{I}&gt;2\sigma(\text{I}) )]</td>
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<tr>
<td>R indices (all data)</td>
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Table A.2. Atomic coordinates and equivalent isotropic displacement parameters (Å² x 10³) for N-pentafluorosulfanyl-1,3-benzothiazol-2-imine (Compound 1).

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<th>Y ( x 10⁴)</th>
<th>Z ( x 10⁴)</th>
<th>U(eq)*</th>
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<td>1304(1)</td>
<td>1935(1)</td>
<td>36(1)</td>
</tr>
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<td>S(2)</td>
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<td>1778(1)</td>
<td>3827(2)</td>
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<tr>
<td>F(1)</td>
<td>2252(4)</td>
<td>1229(2)</td>
<td>1242(3)</td>
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<td>F(2)</td>
<td>6552(4)</td>
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<td>318(2)</td>
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*U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table A.3. Bond lengths and angles for N-pentafluorosulfanyl-1,3-benzothiazol-2-imine (Compound 1).

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<td>C(1)-N(1)</td>
<td>1.318(6)</td>
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<tr>
<td>S(1)-F(2)</td>
<td>1.584(3)</td>
<td>C(3)-C(2)</td>
<td>1.377(8)</td>
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<tr>
<td>S(1)-F(4)</td>
<td>1.586(3)</td>
<td>C(3)-C(4)</td>
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<tr>
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<td>1.589(3)</td>
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<td>S(1)-F(3)</td>
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<td>S(2)-C(1)</td>
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<td>N/A</td>
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<td>N(1)-C(1)-C(2)</td>
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Table A.5. Anisotropic displacement parameters (Å$^2$ x 10$^3$) for N-pentafluorosulfanyl-1,3-benzothiazol-2-imine (Compound 1).

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<td>11(1)</td>
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</table>

The anisotropic displacement factor exponent takes the form: $-2\pi^2[a^2 U_{11} + ... + 2hka^*b^*U_{12}]$.

Table A.6. Hydrogen coordinates and isotropic displacement parameters (Å$^2$ x 10$^3$) for N-pentafluorosulfanyl-1,3-benzothiazol-2-imine (Compound 1).

<table>
<thead>
<tr>
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<th>X ($x 10^4$)</th>
<th>Y ($x 10^4$)</th>
<th>Z ($x 10^4$)</th>
<th>U(eq)</th>
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<tr>
<td>H(2)</td>
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<td>244</td>
<td>5998</td>
<td>42</td>
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<tr>
<td>H(4)</td>
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<td>2178</td>
<td>5316</td>
<td>48</td>
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<td>H(6)</td>
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<td>587</td>
<td>9025</td>
<td>53</td>
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<tr>
<td>H(5)</td>
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<td>1592</td>
<td>7567</td>
<td>55</td>
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<td>H(7)</td>
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<td>88</td>
<td>8197</td>
<td>52</td>
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Table A.7. Torsion angles for *N*-pentafluorosulfonyl-1,3-benzothiazol-2-imine (Compound 1).

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<th>Angle (°)</th>
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</tr>
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<td>178.8(5)</td>
</tr>
<tr>
<td>C(3)-S(2)-C(1)-N(2)</td>
<td>-1.5(4)</td>
</tr>
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<td>N(2)-C(1)-N(1)-S(1)</td>
<td>178.9(4)</td>
</tr>
<tr>
<td>S(2)-C(1)-N(1)-S(1)</td>
<td>-1.5(7)</td>
</tr>
<tr>
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<td>-130.5(5)</td>
</tr>
<tr>
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<td>139.9(5)</td>
</tr>
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<td>49.8(5)</td>
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<td>F(1)-S(1)-N(1)-C(1)</td>
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Figure A.6. H NMR Spectroscopy of N-pentafluorosulfonyl-1,3-benzodioxol-2-imine (Compound 2).
Figure A.7. $^{19}F$ NMR Spectroscopy of N-pentafluorosulfonyl-1,3-benzodioxol-2-imine. (Compound 2)
Figure A.8. $^{13}$C NMR Spectrum of N-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2).
Figure A.9. HRMS of N-pentafluorosulfanyl-1,3-benzodioxol-2-imine. (Compound 2)
Figure A.10. IR Spectrum of N-pentafluorosulfonyl-1,3-benzodioxol-2-imine (Compound 2).
Figure A.11. ORTEP (a), packing structure (b), H···F contact (c), H···N contact (d), and F···F contact (e) of N-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2) crystal structure.
Table A.8. Sample and crystal data collection/refinement for \(N\)-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2).

<table>
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<tr>
<td>Formula weight</td>
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</tr>
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<td>Temperature</td>
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</tr>
<tr>
<td>Wavelength</td>
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</tr>
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<td>Crystal system</td>
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</tr>
<tr>
<td>Space group</td>
<td>(P2_1/c)</td>
</tr>
<tr>
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</tr>
<tr>
<td></td>
<td>(b = 10.9217(7) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(c = 8.8124(5) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(\beta = 103.969(2)^\circ)</td>
</tr>
<tr>
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</tr>
<tr>
<td>Z, Calculated density</td>
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</tr>
<tr>
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<tr>
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<td>Crystal size</td>
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</tr>
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</tr>
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<td>Max. and min. transmission</td>
<td>1.0000 and 0.9302</td>
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<td>Refinement method</td>
<td>Full-matrix least-squares on (F^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2726 / 0 / 145</td>
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<tr>
<td>Goodness-of-fit on (F^2)</td>
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<tr>
<td>R indices (all data)</td>
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<tr>
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Table A.9. Atomic coordinates and equivalent isotropic atomic displacement parameters for N-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2)

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Table A.10. Bond lengths for N-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2).

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<th>Bond length (Å)</th>
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<td>N/A</td>
</tr>
</tbody>
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Table A.11. Bond angles for *N*-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2).

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>Angle (°)</th>
<th>Bond Angle</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F4-S1-F5</td>
<td>89.62(4)</td>
<td>F4-S1-F1</td>
<td>89.84(4)</td>
</tr>
<tr>
<td>F5-S1-F1</td>
<td>174.14(4)</td>
<td>F4-S1-F2</td>
<td>174.59(4)</td>
</tr>
<tr>
<td>F5-S1-F2</td>
<td>89.89(4)</td>
<td>F1-S1-F2</td>
<td>90.10(4)</td>
</tr>
<tr>
<td>F4-S1-F3</td>
<td>87.50(4)</td>
<td>F5-S1-F3</td>
<td>87.20(4)</td>
</tr>
<tr>
<td>F1-S1-F3</td>
<td>86.95(4)</td>
<td>F2-S1-F3</td>
<td>87.10(4)</td>
</tr>
<tr>
<td>F4-S1-N1</td>
<td>90.41(4)</td>
<td>F5-S1-N1</td>
<td>90.19(4)</td>
</tr>
<tr>
<td>F1-S1-N1</td>
<td>95.65(4)</td>
<td>F2-S1-N1</td>
<td>94.98(4)</td>
</tr>
<tr>
<td>F3-S1-N1</td>
<td>176.66(5)</td>
<td>C1-O1-C3</td>
<td>106.14(8)</td>
</tr>
<tr>
<td>C1-O2-C2</td>
<td>106.08(8)</td>
<td>C1-N1-S1</td>
<td>122.87(8)</td>
</tr>
<tr>
<td>N1-C1-O1</td>
<td>129.87(10)</td>
<td>N1-C1-O2</td>
<td>118.09(9)</td>
</tr>
<tr>
<td>O1-C1-O2</td>
<td>112.02(9)</td>
<td>C3-C2-C7</td>
<td>122.95(10)</td>
</tr>
<tr>
<td>C3-C2-O2</td>
<td>107.99(9)</td>
<td>C7-C2-O2</td>
<td>129.03(10)</td>
</tr>
<tr>
<td>C4-C3-C2</td>
<td>123.42(10)</td>
<td>C4-C3-O1</td>
<td>128.85(9)</td>
</tr>
<tr>
<td>C2-C3-O1</td>
<td>107.68(9)</td>
<td>C3-C4-C5</td>
<td>114.81(10)</td>
</tr>
<tr>
<td>C3-C4-H4</td>
<td>122.6</td>
<td>C5-C4-H4</td>
<td>122.6</td>
</tr>
<tr>
<td>C6-C5-C4</td>
<td>122.00(10)</td>
<td>C6-C5-H5</td>
<td>119</td>
</tr>
<tr>
<td>C4-C5-H5</td>
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<td>C5-C6-C7</td>
<td>121.81(10)</td>
</tr>
<tr>
<td>C5-C6-H6</td>
<td>119.1</td>
<td>C7-C6-H6</td>
<td>119.1</td>
</tr>
<tr>
<td>C2-C7-C6</td>
<td>115.01(10)</td>
<td>C2-C7-H7</td>
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</tr>
<tr>
<td>C6-C7-H7</td>
<td>122.5</td>
<td>N/A</td>
<td>N/A</td>
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Table A.12. Anisotropic atomic displacement parameters for N-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$ ($\text{Å}^2$)</th>
<th>$U_{22}$ ($\text{Å}^2$)</th>
<th>$U_{33}$ ($\text{Å}^2$)</th>
<th>$U_{12}$ ($\text{Å}^2$)</th>
<th>$U_{13}$ ($\text{Å}^2$)</th>
<th>$U_{23}$ ($\text{Å}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.01277(14)</td>
<td>0.01544(14)</td>
<td>0.01328(14)</td>
<td>0.00011(8)</td>
<td>0.00184(10)</td>
<td>0.00070(8)</td>
</tr>
<tr>
<td>F1</td>
<td>0.0203(3)</td>
<td>0.0141(3)</td>
<td>0.0253(4)</td>
<td>-0.0010(3)</td>
<td>0.0003(3)</td>
<td>0.0021(2)</td>
</tr>
<tr>
<td>F2</td>
<td>0.0192(4)</td>
<td>0.0329(4)</td>
<td>0.0180(3)</td>
<td>0.0012(3)</td>
<td>0.0081(3)</td>
<td>-0.0047(3)</td>
</tr>
<tr>
<td>F3</td>
<td>0.0179(3)</td>
<td>0.0249(4)</td>
<td>0.0264(4)</td>
<td>-0.0010(3)</td>
<td>-0.0043(3)</td>
<td>-0.0059(3)</td>
</tr>
<tr>
<td>F4</td>
<td>0.0290(4)</td>
<td>0.0283(4)</td>
<td>0.0127(3)</td>
<td>-0.0011(3)</td>
<td>0.0049(3)</td>
<td>-0.0001(3)</td>
</tr>
<tr>
<td>F5</td>
<td>0.0155(3)</td>
<td>0.0213(3)</td>
<td>0.0279(4)</td>
<td>0.00000(3)</td>
<td>-0.0002(3)</td>
<td>0.0062(2)</td>
</tr>
<tr>
<td>O1</td>
<td>0.0140(3)</td>
<td>0.0132(3)</td>
<td>0.0127(3)</td>
<td>0.0020(3)</td>
<td>0.0013(3)</td>
<td>-0.0013(3)</td>
</tr>
<tr>
<td>O2</td>
<td>0.0147(4)</td>
<td>0.0145(3)</td>
<td>0.0179(4)</td>
<td>0.0042(3)</td>
<td>-0.0002(3)</td>
<td>-0.0028(3)</td>
</tr>
<tr>
<td>N1</td>
<td>0.0129(4)</td>
<td>0.0142(4)</td>
<td>0.0155(4)</td>
<td>0.0015(3)</td>
<td>0.0022(3)</td>
<td>-0.0002(3)</td>
</tr>
<tr>
<td>C1</td>
<td>0.0130(4)</td>
<td>0.0119(4)</td>
<td>0.0146(4)</td>
<td>0.0005(3)</td>
<td>0.0046(3)</td>
<td>0.0001(3)</td>
</tr>
<tr>
<td>C2</td>
<td>0.0140(4)</td>
<td>0.0142(4)</td>
<td>0.0135(4)</td>
<td>0.0020(3)</td>
<td>0.0019(4)</td>
<td>0.0001(3)</td>
</tr>
<tr>
<td>C3</td>
<td>0.0126(4)</td>
<td>0.0139(4)</td>
<td>0.0122(4)</td>
<td>-0.0011(3)</td>
<td>0.0032(3)</td>
<td>-0.0007(3)</td>
</tr>
<tr>
<td>C4</td>
<td>0.0180(5)</td>
<td>0.0143(4)</td>
<td>0.0130(4)</td>
<td>0.0011(3)</td>
<td>0.0036(4)</td>
<td>0.0006(4)</td>
</tr>
<tr>
<td>C5</td>
<td>0.0177(5)</td>
<td>0.0206(5)</td>
<td>0.0135(5)</td>
<td>0.0024(4)</td>
<td>0.0024(4)</td>
<td>0.0016(4)</td>
</tr>
<tr>
<td>C6</td>
<td>0.0152(5)</td>
<td>0.0251(6)</td>
<td>0.0157(5)</td>
<td>0.0018(4)</td>
<td>0.0012(4)</td>
<td>-0.0023(4)</td>
</tr>
<tr>
<td>C7</td>
<td>0.0156(5)</td>
<td>0.0197(5)</td>
<td>0.0186(5)</td>
<td>0.0019(4)</td>
<td>0.0017(4)</td>
<td>-0.0046(4)</td>
</tr>
</tbody>
</table>

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 \alpha^2 U_{11} + \ldots + 2hk\alpha^*\beta^*U_{12}].$

Table A.13. Hydrogen atomic coordinates and isotropic atomic displacement parameters for N-pentafluorosulfanyl-1,3-benzodioxol-2-imine (Compound 2).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq) $(\text{Å}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H4</td>
<td>0.3465</td>
<td>0.5559</td>
<td>-0.0037</td>
<td>0.018</td>
</tr>
<tr>
<td>H5</td>
<td>0.1203</td>
<td>0.4939</td>
<td>-0.1612</td>
<td>0.021</td>
</tr>
<tr>
<td>H6</td>
<td>0.0191</td>
<td>0.307</td>
<td>-0.1215</td>
<td>0.023</td>
</tr>
<tr>
<td>H7</td>
<td>0.136</td>
<td>0.1731</td>
<td>0.0817</td>
<td>0.022</td>
</tr>
</tbody>
</table>
Figure A.12. $^1$H NMR Spectrum of N-pentafluorosulfanyl-1,3-benoxazol-2-imine (Compound 3).
Figure A.13. \(^{19}F\) NMR Spectrum of \(N\)-pentafluorosulfanyl-1,3-benoxazol-2-imine (Compound 3).
Figure A.14. $^{13}$C NMR Spectrum of N-pentafluorosulfonyl-1,3-benzoxazol-2-imine (Compound 3).
Figure A.15. HRMS of $N$-pentafluorosulfanyl-1,3-benzoxazol-2-imine (Compound 3).
Figure A.16. IR Spectrum of N-pentafluorosulfanyl-1,3-benoxazol-2-imine (Compound 3).
Figure A.17. ORTEP (a), packing structure (b), H···N contact (c), and F···F contact (d), of N-pentafluorosulfanyl-1,3-benzoxazol-2-imine (Compound 3).
<table>
<thead>
<tr>
<th>Identification Code</th>
<th>N-pentafluorosulfanyl-1,3-benoxazol-2-imine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C\textsubscript{7}H\textsubscript{5}F\textsubscript{5}N\textsubscript{2}OS</td>
</tr>
<tr>
<td>Formula weight</td>
<td>260.19 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.085x0.122x 0.222 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P\textsubscript{2}1/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>\begin{align*} a &amp;= 9.6658(6) \text{ Å} \ b &amp;= 5.5708(3) \text{ Å} \ c &amp;= 16.2962(10) \text{ Å} \ \beta &amp;= 90.505(2)° \end{align*}</td>
</tr>
<tr>
<td>Volume</td>
<td>877.45(9) Å\textsuperscript{3}</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.970 g/cm\textsuperscript{3}</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.431 mm\textsuperscript{-1}</td>
</tr>
<tr>
<td>F(000)</td>
<td>520</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.44° to 26.50°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-12&lt;=h&lt;=12, -6&lt;=k&lt;=6, -20&lt;=l&lt;=20</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>25619</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1804 [R\text{int} = 0.0358]</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9640 and 0.9100</td>
</tr>
<tr>
<td>Structure solution technique</td>
<td>direct methods</td>
</tr>
<tr>
<td>Structure solution program</td>
<td>XT, VERSION 2014/4</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F\textsuperscript{2}</td>
</tr>
<tr>
<td>Refinement program</td>
<td>SHELXL-2014/7 (Sheldrick, 2014)</td>
</tr>
<tr>
<td>Function minimized</td>
<td>(\Sigma w(F_o^2 - F_c^2)^2)</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>1804 / 0 / 145</td>
</tr>
<tr>
<td>Goodness-of-fit on F\textsuperscript{2}</td>
<td>1.189</td>
</tr>
<tr>
<td>Final R indices</td>
<td>\begin{align*} \text{all data} R1 &amp;= 0.0510, wR2 = 0.1619 \ \text{l}&gt;2\sigma(l) \ R1 &amp;= 0.0374, wR2 = 0.1192 \end{align*}</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>(w = 1/[\sigma^2(F_o^2)+(0.0907P)^2+1.8361P]) where (P = (F_o^2 + 2F_c^2)/3)</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.0(0)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.071 and -0.942 eÅ\textsuperscript{-3}</td>
</tr>
<tr>
<td>R.M.S. deviation from mean</td>
<td>0.371 eÅ\textsuperscript{-3}</td>
</tr>
</tbody>
</table>
Table A.15. Atomic coordinates and equivalent isotropic atomic displacement parameters for \( N \)-pentafluorosulfanyl-1,3-benoxazol-2-imine (Compound 3).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)* (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.77406(7)</td>
<td>0.39811(12)</td>
<td>0.87658(4)</td>
<td>0.0115(3)</td>
</tr>
<tr>
<td>F1</td>
<td>0.90611(18)</td>
<td>0.3840(3)</td>
<td>0.93382(11)</td>
<td>0.0184(4)</td>
</tr>
<tr>
<td>F2</td>
<td>0.8158(2)</td>
<td>0.6618(3)</td>
<td>0.84935(11)</td>
<td>0.0201(4)</td>
</tr>
<tr>
<td>F3</td>
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<td>0.3050(4)</td>
<td>0.80438(11)</td>
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</tr>
<tr>
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<td>0.4019(3)</td>
<td>0.81047(11)</td>
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</tr>
<tr>
<td>F5</td>
<td>0.7389(2)</td>
<td>0.1270(3)</td>
<td>0.89429(12)</td>
<td>0.0212(5)</td>
</tr>
<tr>
<td>O1</td>
<td>0.8127(2)</td>
<td>0.7740(4)</td>
<td>0.01225(12)</td>
<td>0.0109(4)</td>
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<tr>
<td>N1</td>
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<td>0.4846(4)</td>
<td>0.94846(14)</td>
<td>0.0115(5)</td>
</tr>
<tr>
<td>N2</td>
<td>0.5932(2)</td>
<td>0.7524(4)</td>
<td>0.04831(15)</td>
<td>0.0115(5)</td>
</tr>
<tr>
<td>C1</td>
<td>0.6912(3)</td>
<td>0.6599(5)</td>
<td>0.99945(16)</td>
<td>0.0101(6)</td>
</tr>
<tr>
<td>C2</td>
<td>0.6505(3)</td>
<td>0.9381(5)</td>
<td>0.09463(16)</td>
<td>0.0111(6)</td>
</tr>
<tr>
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<td>0.9510(5)</td>
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<td>0.0105(6)</td>
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<tr>
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<tr>
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<td>0.0158(6)</td>
</tr>
<tr>
<td>C6</td>
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<td>0.2715(5)</td>
<td>0.18189(17)</td>
<td>0.0157(6)</td>
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<tr>
<td>C7</td>
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<td>0.0998(5)</td>
<td>0.15050(17)</td>
<td>0.0135(6)</td>
</tr>
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</table>

*U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table A.16. Bond lengths for \( N \)-pentafluorosulfanyl-1,3-benoxazol-2-imine (Compound 3).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond length (Å)</th>
<th>Bond</th>
<th>Bond length (Å)</th>
</tr>
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<tbody>
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<td>1.5756(19)</td>
<td>S1-F1</td>
<td>1.5763(18)</td>
</tr>
<tr>
<td>S1-F2</td>
<td>1.5878(19)</td>
<td>S1-F4</td>
<td>1.5918(19)</td>
</tr>
<tr>
<td>S1-F3</td>
<td>1.5972(18)</td>
<td>S1-N1</td>
<td>1.646(2)</td>
</tr>
<tr>
<td>O1-C1</td>
<td>1.351(3)</td>
<td>O1-C3</td>
<td>1.402(3)</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.303(4)</td>
<td>N2-C1</td>
<td>1.345(4)</td>
</tr>
<tr>
<td>N2-C2</td>
<td>1.393(4)</td>
<td>N2-H2</td>
<td>0.88</td>
</tr>
<tr>
<td>C2-C7</td>
<td>1.388(4)</td>
<td>C2-C3</td>
<td>1.390(4)</td>
</tr>
<tr>
<td>C3-C4</td>
<td>1.371(4)</td>
<td>C4-C5</td>
<td>1.394(4)</td>
</tr>
<tr>
<td>C4-H4</td>
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<td>C5-C6</td>
<td>1.399(4)</td>
</tr>
<tr>
<td>C5-H5</td>
<td>0.95</td>
<td>C6-C7</td>
<td>1.393(4)</td>
</tr>
<tr>
<td>C6-H6</td>
<td>0.95</td>
<td>C7-H7</td>
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</table>
Table A.17. Bond angles for N-pentafluorosulfanyl-1,3-benoxazol-2-imine (Compound 3).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F5-S1-F1</td>
<td>91.06(11)</td>
<td>F5-S1-F2</td>
<td>173.73(10)</td>
</tr>
<tr>
<td>F1-S1-F2</td>
<td>90.28(10)</td>
<td>F5-S1-F4</td>
<td>88.67(11)</td>
</tr>
<tr>
<td>F1-S1-F4</td>
<td>173.40(10)</td>
<td>F2-S1-F4</td>
<td>89.29(10)</td>
</tr>
<tr>
<td>F5-S1-F3</td>
<td>87.28(11)</td>
<td>F1-S1-F3</td>
<td>86.70(10)</td>
</tr>
<tr>
<td>F2-S1-F3</td>
<td>86.68(10)</td>
<td>F4-S1-F3</td>
<td>86.70(11)</td>
</tr>
<tr>
<td>F5-S1-N1</td>
<td>90.66(12)</td>
<td>F1-S1-N1</td>
<td>96.18(11)</td>
</tr>
<tr>
<td>F2-S1-N1</td>
<td>95.29(11)</td>
<td>F4-S1-N1</td>
<td>90.42(11)</td>
</tr>
<tr>
<td>F3-S1-N1</td>
<td>176.49(12)</td>
<td>C1-O1-C3</td>
<td>106.6(2)</td>
</tr>
<tr>
<td>C1-N1-S1</td>
<td>124.0(2)</td>
<td>C1-N2-C2</td>
<td>109.1(2)</td>
</tr>
<tr>
<td>C1-N2-H2</td>
<td>125.5</td>
<td>C2-N2-H2</td>
<td>125.5</td>
</tr>
<tr>
<td>N1-C1-N2</td>
<td>122.5(2)</td>
<td>N1-C1-O1</td>
<td>127.3(2)</td>
</tr>
<tr>
<td>N2-C1-O1</td>
<td>110.1(2)</td>
<td>C7-C2-C3</td>
<td>120.9(3)</td>
</tr>
<tr>
<td>C7-C2-N2</td>
<td>133.4(3)</td>
<td>C3-C2-N2</td>
<td>105.6(2)</td>
</tr>
<tr>
<td>C4-C3-C2</td>
<td>123.7(3)</td>
<td>C4-C3-O1</td>
<td>127.8(3)</td>
</tr>
<tr>
<td>C2-C3-O1</td>
<td>108.5(2)</td>
<td>C3-C4-C5</td>
<td>115.5(3)</td>
</tr>
<tr>
<td>C3-C4-H4</td>
<td>122.2</td>
<td>C5-C4-H4</td>
<td>122.2</td>
</tr>
<tr>
<td>C4-C5-C6</td>
<td>121.8(3)</td>
<td>C4-C5-H5</td>
<td>119.1</td>
</tr>
<tr>
<td>C6-C5-H5</td>
<td>119.1</td>
<td>C7-C6-C5</td>
<td>121.7(3)</td>
</tr>
<tr>
<td>C7-C6-H6</td>
<td>119.2</td>
<td>C5-C6-H6</td>
<td>119.2</td>
</tr>
<tr>
<td>C2-C7-C6</td>
<td>116.4(3)</td>
<td>C2-C7-H7</td>
<td>121.8</td>
</tr>
<tr>
<td>C6-C7-H7</td>
<td>121.8</td>
<td></td>
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</tbody>
</table>
Table A.18. Anisotropic atomic displacement parameters for N-pentafluorosulfanyl-1,3-benzoxazol-2-imine (Compound 3).

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$ (Å²)</th>
<th>$U_{22}$ (Å²)</th>
<th>$U_{33}$ (Å²)</th>
<th>$U_{23}$ (Å²)</th>
<th>$U_{13}$ (Å²)</th>
<th>$U_{12}$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0113(4)</td>
<td>0.0103(4)</td>
<td>0.0130(4)</td>
<td>-0.0033(2)</td>
<td>0.0024(3)</td>
<td>-0.0006(2)</td>
</tr>
<tr>
<td>F1</td>
<td>0.0119(9)</td>
<td>0.0233(10)</td>
<td>0.0199(9)</td>
<td>-0.0032(7)</td>
<td>-0.0027(7)</td>
<td>0.0040(7)</td>
</tr>
<tr>
<td>F2</td>
<td>0.0273(10)</td>
<td>0.0156(9)</td>
<td>0.0173(9)</td>
<td>0.0027(7)</td>
<td>0.0042(7)</td>
<td>-0.0045(8)</td>
</tr>
<tr>
<td>F3</td>
<td>0.0245(10)</td>
<td>0.0249(10)</td>
<td>0.0199(10)</td>
<td>-0.0082(8)</td>
<td>0.0095(8)</td>
<td>-0.0020(8)</td>
</tr>
<tr>
<td>F4</td>
<td>0.0242(10)</td>
<td>0.0232(10)</td>
<td>0.0162(9)</td>
<td>-0.0044(7)</td>
<td>-0.0049(7)</td>
<td>-0.0006(8)</td>
</tr>
<tr>
<td>F5</td>
<td>0.0274(10)</td>
<td>0.0092(9)</td>
<td>0.0270(10)</td>
<td>-0.0020(7)</td>
<td>0.0057(8)</td>
<td>0.0003(7)</td>
</tr>
<tr>
<td>O1</td>
<td>0.0094(9)</td>
<td>0.0115(10)</td>
<td>0.0117(9)</td>
<td>-0.0033(7)</td>
<td>0.0014(7)</td>
<td>-0.0025(7)</td>
</tr>
<tr>
<td>N1</td>
<td>0.0076(11)</td>
<td>0.0130(12)</td>
<td>0.0141(12)</td>
<td>-0.0034(9)</td>
<td>0.0028(8)</td>
<td>-0.0010(9)</td>
</tr>
<tr>
<td>N2</td>
<td>0.0088(11)</td>
<td>0.0116(12)</td>
<td>0.0140(11)</td>
<td>-0.0032(9)</td>
<td>0.0023(9)</td>
<td>-0.0024(9)</td>
</tr>
<tr>
<td>C1</td>
<td>0.0094(13)</td>
<td>0.0099(13)</td>
<td>0.0109(12)</td>
<td>0.0011(10)</td>
<td>0.0003(10)</td>
<td>0.0005(10)</td>
</tr>
<tr>
<td>C2</td>
<td>0.0127(13)</td>
<td>0.0098(13)</td>
<td>0.0108(12)</td>
<td>0.0003(10)</td>
<td>0.0005(10)</td>
<td>0.0020(10)</td>
</tr>
<tr>
<td>C3</td>
<td>0.0131(13)</td>
<td>0.0105(13)</td>
<td>0.0080(12)</td>
<td>0.0017(10)</td>
<td>0.0030(10)</td>
<td>0.0002(10)</td>
</tr>
<tr>
<td>C4</td>
<td>0.0145(14)</td>
<td>0.0179(15)</td>
<td>0.0127(13)</td>
<td>0.0008(11)</td>
<td>0.0010(11)</td>
<td>0.0045(11)</td>
</tr>
<tr>
<td>C5</td>
<td>0.0211(15)</td>
<td>0.0145(14)</td>
<td>0.0120(13)</td>
<td>0.0028(11)</td>
<td>0.0035(11)</td>
<td>0.0073(12)</td>
</tr>
<tr>
<td>C6</td>
<td>0.0222(15)</td>
<td>0.0134(14)</td>
<td>0.0114(13)</td>
<td>0.0021(10)</td>
<td>0.0031(11)</td>
<td>0.0006(12)</td>
</tr>
<tr>
<td>C7</td>
<td>0.0145(14)</td>
<td>0.0142(14)</td>
<td>0.0118(13)</td>
<td>0.0012(10)</td>
<td>0.0028(10)</td>
<td>0.0003(11)</td>
</tr>
</tbody>
</table>

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^{2}[ h^2 a^2 U_{11} + ... + 2 h k a^* b^* U_{12}]$.

Table A.19. Hydrogen atomic coordinates and isotropic atomic displacement parameters for N-pentafluorosulfanyl-1,3-benzoxazol-2-imine (Compound 3).

<table>
<thead>
<tr>
<th>Atom</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.5068</td>
<td>-0.2965</td>
<td>0.0506</td>
<td>0.014</td>
</tr>
<tr>
<td>H4</td>
<td>0.9739</td>
<td>0.1226</td>
<td>0.0854</td>
<td>0.018</td>
</tr>
<tr>
<td>H5</td>
<td>0.8847</td>
<td>0.3987</td>
<td>0.1815</td>
<td>0.019</td>
</tr>
<tr>
<td>H6</td>
<td>0.654</td>
<td>0.3859</td>
<td>0.2202</td>
<td>0.019</td>
</tr>
<tr>
<td>H7</td>
<td>0.5019</td>
<td>0.0937</td>
<td>0.1665</td>
<td>0.016</td>
</tr>
</tbody>
</table>
Table A.20. Hydrogen bond distances and angles for N-pentafluorosulfanyl-1,3-benzoazol-2-imine (Compound 3).

<table>
<thead>
<tr>
<th></th>
<th>Donor-H (Å)</th>
<th>Acceptor-H (Å)</th>
<th>Donor-Acceptor (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-H2···S1</td>
<td>0.88</td>
<td>3.03</td>
<td>3.858(2)</td>
<td>158.5</td>
</tr>
<tr>
<td>N2-H2···N1</td>
<td>0.88</td>
<td>1.97</td>
<td>2.836(3)</td>
<td>165.9</td>
</tr>
<tr>
<td>C4-H4···F2</td>
<td>0.95</td>
<td>2.58</td>
<td>3.278(4)</td>
<td>130.4</td>
</tr>
</tbody>
</table>
Figure A.18. $^1$H NMR Spectrum of 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).
Figure A.19. $^{19}\text{F}$ NMR Spectrum of 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).
Figure A.20. IR Spectrum of 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).
Figure A.21. ORTEP (a), packing structure (b), H···F contact (c), and F···F contact (d), of 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).
Table A. 21 Sample and crystal data for 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).

<table>
<thead>
<tr>
<th>Identification code</th>
<th>4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₇H₁₂F₅NO₂S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>269.24 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.089x0.091x0.314 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₁</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 6.8947(9) Å, α = 86.439(4)°, b = 8.3596(12) Å, β = 83.879(3)°, c = 9.5181(13) Å, γ = 79.838(3)°</td>
</tr>
<tr>
<td>Volume</td>
<td>536.38(13) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.667 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.359 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>276</td>
</tr>
</tbody>
</table>

Table A. 22. Data collection and structure refinement for 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).

<table>
<thead>
<tr>
<th>Theta range for data collection</th>
<th>2.48° to 25.99°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflections collected</td>
<td>2112</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2112 [R_{int}= 0.0430]</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.0000 and 0.9400</td>
</tr>
<tr>
<td>Structure solution technique</td>
<td>direct methods</td>
</tr>
<tr>
<td>Structure solution program</td>
<td>SHELXT-2014 (Sheldrick 2014)</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Refinement program</td>
<td>SHELXL-2014 (Sheldrick 2014)</td>
</tr>
<tr>
<td>Function minimized</td>
<td>Σw(F_o²-F_c²)^2</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2112 / 0 / 146</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.114</td>
</tr>
<tr>
<td>Final R indices</td>
<td>1849 data; l&gt;2σ(l) R1 = 0.0346, wR2 = 0.0763</td>
</tr>
</tbody>
</table>
Table A.23. Atomic coordinates and equivalent isotropic atomic displacement parameters for 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).

<table>
<thead>
<tr>
<th>S1</th>
<th>0.01101(7)</th>
<th>0.26560(6)</th>
<th>0.23842(6)</th>
<th>0.02268(15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>0.00353(19)</td>
<td>0.13664(15)</td>
<td>0.12552(14)</td>
<td>0.0331(3)</td>
</tr>
<tr>
<td>F2</td>
<td>0.9865(2)</td>
<td>0.13117(15)</td>
<td>0.36046(14)</td>
<td>0.0341(3)</td>
</tr>
<tr>
<td>F3</td>
<td>0.04341(19)</td>
<td>0.38650(15)</td>
<td>0.35229(14)</td>
<td>0.0335(3)</td>
</tr>
<tr>
<td>F4</td>
<td>0.06143(18)</td>
<td>0.39123(15)</td>
<td>0.11487(14)</td>
<td>0.0327(3)</td>
</tr>
<tr>
<td>F5</td>
<td>0.24381(18)</td>
<td>0.19870(16)</td>
<td>0.23181(16)</td>
<td>0.0379(4)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>O1</td>
<td>0.4891(2)</td>
<td>0.50368(16)</td>
<td>0.26481(16)</td>
<td>0.0229(3)</td>
</tr>
<tr>
<td>O2</td>
<td>0.7669(2)</td>
<td>0.60366(16)</td>
<td>0.23149(16)</td>
<td>0.0224(3)</td>
</tr>
<tr>
<td>N1</td>
<td>0.7686(2)</td>
<td>0.3219(2)</td>
<td>0.24633(18)</td>
<td>0.0213(4)</td>
</tr>
<tr>
<td>C1</td>
<td>0.6853(3)</td>
<td>0.4717(2)</td>
<td>0.2471(2)</td>
<td>0.0184(4)</td>
</tr>
<tr>
<td>C2</td>
<td>0.4250(3)</td>
<td>0.6807(2)</td>
<td>0.2366(2)</td>
<td>0.0214(4)</td>
</tr>
<tr>
<td>C3</td>
<td>0.6102(3)</td>
<td>0.7451(2)</td>
<td>0.2702(2)</td>
<td>0.0214(4)</td>
</tr>
<tr>
<td>C4</td>
<td>0.2401(3)</td>
<td>0.7324(3)</td>
<td>0.3348(3)</td>
<td>0.0344(6)</td>
</tr>
<tr>
<td>C5</td>
<td>0.3836(4)</td>
<td>0.7027(3)</td>
<td>0.0831(3)</td>
<td>0.0351(6)</td>
</tr>
<tr>
<td>C6</td>
<td>0.6601(3)</td>
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<td>0.1802(3)</td>
<td>0.0345(6)</td>
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<tr>
<td>C7</td>
<td>0.6199(4)</td>
<td>0.7676(3)</td>
<td>0.4257(3)</td>
<td>0.0389(6)</td>
</tr>
</tbody>
</table>

*U(eq)* is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table A.24. Bond lengths for 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).
Table A.25. Bond angles for 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).

<table>
<thead>
<tr>
<th>Bonding Atoms</th>
<th>Bond angle (°)</th>
<th>Bonding Atoms</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F4-S1-F1</td>
<td>89.70(8)</td>
<td>F4-S1-F2</td>
<td>173.45(7)</td>
</tr>
<tr>
<td>F1-S1-F2</td>
<td>89.44(7)</td>
<td>F4-S1-F3</td>
<td>90.53(8)</td>
</tr>
<tr>
<td>F1-S1-F3</td>
<td>173.69(8)</td>
<td>F2-S1-F3</td>
<td>89.62(8)</td>
</tr>
<tr>
<td>F4-S1-F5</td>
<td>86.80(7)</td>
<td>F1-S1-F5</td>
<td>86.70(7)</td>
</tr>
<tr>
<td>F2-S1-F5</td>
<td>86.67(7)</td>
<td>F3-S1-F5</td>
<td>87.02(7)</td>
</tr>
<tr>
<td>F4-S1-N1</td>
<td>96.03(8)</td>
<td>F1-S1-N1</td>
<td>90.74(8)</td>
</tr>
<tr>
<td>F2-S1-N1</td>
<td>90.47(8)</td>
<td>F3-S1-N1</td>
<td>95.50(8)</td>
</tr>
<tr>
<td>F5-S1-N1</td>
<td>176.18(8)</td>
<td>C1-O1-C2</td>
<td>108.21(14)</td>
</tr>
<tr>
<td>C1-O2-C3</td>
<td>107.89(14)</td>
<td>C1-N1-S1</td>
<td>122.36(15)</td>
</tr>
<tr>
<td>N1-C1-O2</td>
<td>129.24(19)</td>
<td>N1-C1-O1</td>
<td>117.59(17)</td>
</tr>
<tr>
<td>O2-C1-O1</td>
<td>113.16(17)</td>
<td>O1-C2-C5</td>
<td>106.63(17)</td>
</tr>
</tbody>
</table>
Table A.26. Torsion angles for 4,4,5,5-tetramethyl- N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).
Table A.27. Anisotropic atomic displacement parameters for 4,4,5,5-tetramethyl-
N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4). The anisotropic atomic

displacement factor exponent takes the form: $-2\pi^2(h^2a^2U_{11} + \ldots + 2hkab'U_{12})$

<table>
<thead>
<tr>
<th></th>
<th>$U_{11}$ (Å$^2$)</th>
<th>$U_{22}$ (Å$^2$)</th>
<th>$U_{33}$ (Å$^2$)</th>
<th>$U_{23}$ (Å$^2$)</th>
<th>$U_{13}$ (Å$^2$)</th>
<th>$U_{12}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0208(3)</td>
<td>0.0171(3)</td>
<td>0.0278(3)</td>
<td>-0.0001(2)</td>
<td>-0.0008(2)</td>
<td>0.00193(19)</td>
</tr>
<tr>
<td>F1</td>
<td>0.0338(7)</td>
<td>0.0262(7)</td>
<td>0.0365(8)</td>
<td>-0.0107(6)</td>
<td>0.0029(6)</td>
<td>0.0018(6)</td>
</tr>
<tr>
<td>F2</td>
<td>0.0392(8)</td>
<td>0.0225(7)</td>
<td>0.0343(8)</td>
<td>0.0078(6)</td>
<td>0.0005(6)</td>
<td>0.0064(6)</td>
</tr>
<tr>
<td>F3</td>
<td>0.0304(7)</td>
<td>0.0288(7)</td>
<td>0.0421(8)</td>
<td>-0.0081(6)</td>
<td>-0.0152(6)</td>
<td>0.0024(6)</td>
</tr>
<tr>
<td>F4</td>
<td>0.0263(7)</td>
<td>0.0281(7)</td>
<td>0.0393(8)</td>
<td>0.0082(6)</td>
<td>0.0060(6)</td>
<td>-0.0017(5)</td>
</tr>
<tr>
<td>F5</td>
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<td>0.0561(9)</td>
<td>-0.0005(7)</td>
<td>-0.0034(6)</td>
<td>0.0071(6)</td>
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<tr>
<td>O1</td>
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<td>0.0160(7)</td>
<td>0.0354(9)</td>
<td>0.0009(6)</td>
<td>0.0000(6)</td>
<td>-0.0009(5)</td>
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<td>-0.0005(6)</td>
</tr>
<tr>
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<td>-0.0008(7)</td>
<td>-0.0007(7)</td>
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<tr>
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<td>-0.0006(8)</td>
<td>-0.0041(8)</td>
</tr>
<tr>
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<td>0.0147(9)</td>
<td>0.0290(12)</td>
<td>0.0003(8)</td>
<td>-0.0017(8)</td>
<td>0.0002(8)</td>
</tr>
<tr>
<td>C3</td>
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<td>0.0156(9)</td>
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<td>-0.0019(9)</td>
<td>0.0014(8)</td>
</tr>
<tr>
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<td>0.0260(12)</td>
<td>0.0509(15)</td>
<td>0.0011(11)</td>
<td>0.0077(11)</td>
<td>0.0022(9)</td>
</tr>
<tr>
<td>C5</td>
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<td>0.0319(12)</td>
<td>0.0362(14)</td>
<td>0.0002(10)</td>
<td>0.0147(11)</td>
<td>0.0010(10)</td>
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<tr>
<td>C6</td>
<td>0.0255(12)</td>
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<td>0.0005(11)</td>
<td>-0.0022(9)</td>
</tr>
<tr>
<td>C7</td>
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<td>0.0337(13)</td>
<td>0.0371(14)</td>
<td>0.0121(11)</td>
<td>0.0132(12)</td>
<td>0.0017(11)</td>
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Table A.28. Hydrogen atomic coordinates and isotropic atomic displacement parameters

for 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).

<table>
<thead>
<tr>
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<th>x/a</th>
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<th>z/c</th>
<th>U(eq) (Å$^2$)</th>
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<tbody>
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<td>0.193</td>
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<td>0.3193</td>
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</tr>
<tr>
<td>H4B</td>
<td>0.1372</td>
<td>0.6717</td>
<td>0.3156</td>
<td>0.052</td>
</tr>
<tr>
<td>H4C</td>
<td>0.2702</td>
<td>0.7099</td>
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<td>0.052</td>
</tr>
<tr>
<td>H5A</td>
<td>0.3405</td>
<td>0.8184</td>
<td>0.0596</td>
<td>0.053</td>
</tr>
<tr>
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<td>0.6619</td>
<td>0.0228</td>
<td>0.053</td>
</tr>
<tr>
<td>H5C</td>
<td>0.279</td>
<td>0.642</td>
<td>0.0674</td>
<td>0.053</td>
</tr>
<tr>
<td>H6A</td>
<td>0.5598</td>
<td>0.9859</td>
<td>0.2029</td>
<td>0.052</td>
</tr>
<tr>
<td>H6B</td>
<td>0.7903</td>
<td>0.9107</td>
<td>0.1993</td>
<td>0.052</td>
</tr>
<tr>
<td>H6C</td>
<td>0.6628</td>
<td>0.8681</td>
<td>0.0801</td>
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</tr>
<tr>
<td>H7A</td>
<td>0.5192</td>
<td>0.8598</td>
<td>0.4572</td>
<td>0.058</td>
</tr>
<tr>
<td>H7B</td>
<td>0.5953</td>
<td>0.6687</td>
<td>0.4804</td>
<td>0.058</td>
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</table>
Table A.29. Hydrogen bond distances and angles for 4,4,5,5-tetramethyl-N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 4).

<table>
<thead>
<tr>
<th>Donor-H</th>
<th>Acceptor-H</th>
<th>Donor-Acceptor (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-H4A</td>
<td>F2</td>
<td>3.490(3)</td>
<td>158.7</td>
</tr>
<tr>
<td>C4-H4B</td>
<td>F3</td>
<td>3.391(3)</td>
<td>141.2</td>
</tr>
<tr>
<td>C6-H6A</td>
<td>F5</td>
<td>3.518(3)</td>
<td>165.9</td>
</tr>
<tr>
<td>C6-H6B</td>
<td>F1</td>
<td>3.383(3)</td>
<td>135.8</td>
</tr>
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</table>
Figure A.22. $^{19}$F NMR Spectrum of $N$-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).
Figure A.23. HRMS of $N$-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).
Figure A.24. IR Spectrum of N-pentafluorosulfonyl-1,3-dioxolan-2-imine (Compound 5).
Figure A.25. ORTEP (a), packing structure (b), F···F contact (c), H···O contact (d), and H···F contact (e) of N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).
Table A.30. Sample and crystal data for N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).

<table>
<thead>
<tr>
<th>Identification code</th>
<th>N-pentafluorosulfanyl-1,3-dioxolan-2-imine</th>
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</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₃H₄F₅NO₂S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>213.13 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.306x0.326x0.443 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₂₁/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a= 7.4353(5) Å, b= 14.8688(10) Å, c= 6.0447(4) Å, β= 99.8953(18)°</td>
</tr>
<tr>
<td>Volume</td>
<td>658.32(8) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>2.150 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.554 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>424</td>
</tr>
</tbody>
</table>

Table A.31. Data collection and structure refinement for N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).

| Theta range for data collection | 2.74° to 27.49° |
| Index ranges                   | -9<=h<=9, -19<=k<=19, -7<=l<=7      |
| Reflections collected          | 11022                                   |
| Independent reflections        | 1498 [Rint= 0.0317]                     |
| Max. and min. transmission     | 0.8490 and 0.7920                        |
| Structure solution technique   | direct methods                          |
| Structure solution program     | XS, VERSION 2013/1                      |
| Refinement method              | Full-matrix least-squares on F²        |
| Refinement program             | SHELXL-2014/7 (Sheldrick, 2014)         |
| Function minimized             | $\Sigma w(F_o^2-F_c^2)^2$               |
| Data / restraints / parameters | 1498 / 0 / 109                           |
| Goodness-of-fit on F²          | 1.146                                    |
| Final R indices                | 1469 data; l>2σ(l) R1= 0.0267, wR2= 0.0705 |
| all data; R1 = 0.0271, wR2 = 0.0708 |
| Weighting scheme               | $w=1/[σ^2(F_o^2)+(0.0325P)^2+0.4396P]$   |
| where P=$(F_o^2+2F_c^2)/3$      |
| Largest diff. peak and hole    | 0.489 and -0.531 eÅ⁻³                  |
| R.M.S. deviation from mean     | 0.059 eÅ⁻³                              |
Table A.32. Atomic coordinates and equivalent isotropic atomic displacement parameters for N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)* (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.27587(4)</td>
<td>0.11575(2)</td>
<td>0.07827(5)</td>
<td>0.01064(11)</td>
</tr>
<tr>
<td>F5</td>
<td>0.33071(11)</td>
<td>0.12338(6)</td>
<td>0.83678(14)</td>
<td>0.01539(19)</td>
</tr>
<tr>
<td>F4</td>
<td>0.20720(11)</td>
<td>0.01524(5)</td>
<td>0.02239(14)</td>
<td>0.01488(19)</td>
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<tr>
<td>F3</td>
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<td>0.07323(6)</td>
<td>0.15989(14)</td>
<td>0.0177(2)</td>
</tr>
<tr>
<td>F2</td>
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<td>0.10291(6)</td>
<td>0.32849(14)</td>
<td>0.0194(2)</td>
</tr>
<tr>
<td>O2</td>
<td>0.80275(13)</td>
<td>0.18563(7)</td>
<td>0.78928(16)</td>
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</tr>
<tr>
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<tr>
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<tr>
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<td>0.01127(19)</td>
<td>0.0127(2)</td>
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<tr>
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<td>0.8259(2)</td>
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<tr>
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<td>0.0138(3)</td>
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<tr>
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<td>0.10201(9)</td>
<td>0.4746(2)</td>
<td>0.0130(3)</td>
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</table>

*U(eq) is defined as one third of the trace of the orthogonalized \( U_{ij} \) tensor.

Table A.33. Bond lengths for N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).

<table>
<thead>
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<th>Bond</th>
<th>Bond lengths (Å)</th>
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<tbody>
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<td>S1-F2</td>
<td>1.5818(9)</td>
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<tr>
<td>S1-F5</td>
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<td>S1-F4</td>
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<tr>
<td>S1-F3</td>
<td>1.6072(8)</td>
<td>S1-N1</td>
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<tr>
<td>O2-C1</td>
<td>1.3341(16)</td>
<td>O2-C3</td>
<td>1.4584(16)</td>
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<tr>
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<td>O1-C2</td>
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<td>1.2817(17)</td>
<td>C3-C2</td>
<td>1.5185(18)</td>
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<tr>
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<tr>
<td>C2-H2A</td>
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Table A.34. Bond angles for N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).
<table>
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<tr>
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<th>Bonding Atoms</th>
<th>Bond Angle (°)</th>
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</tr>
<tr>
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</tr>
<tr>
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<td>F5-S1-F4</td>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
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<td>108.45(10)</td>
<td>C1-N1-S1</td>
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<tr>
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<tr>
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Table A.35. Anisotropic atomic displacement parameters (Å²) for N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).

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<th>(U_{33}(\text{Å}^2))</th>
<th>(U_{23}(\text{Å}^2))</th>
<th>(U_{13}(\text{Å}^2))</th>
<th>(U_{12}(\text{Å}^2))</th>
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<tbody>
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<tr>
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<td>0.0071(3)</td>
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</tr>
<tr>
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<td>0.0104(4)</td>
<td>0.0176(4)</td>
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<td>0.0014(3)</td>
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</tr>
<tr>
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<td>0.0024(4)</td>
<td>0.0045(4)</td>
</tr>
<tr>
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<td>0.0258(5)</td>
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<td>0.0011(3)</td>
<td>-0.0051(3)</td>
</tr>
<tr>
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<td>0.0095(4)</td>
<td>-0.0020(3)</td>
<td>0.0016(3)</td>
<td>0.0028(3)</td>
</tr>
<tr>
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<td>0.0127(5)</td>
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<td>0.0037(4)</td>
<td>0.0020(4)</td>
</tr>
<tr>
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<td>0.0084(5)</td>
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<td>-0.0001(4)</td>
</tr>
<tr>
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<td>0.0162(6)</td>
<td>0.0128(6)</td>
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<td>0.0018(5)</td>
<td>0.0015(5)</td>
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<td>0.0104(6)</td>
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<td>0.0041(5)</td>
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</tbody>
</table>

The anisotropic atomic displacement factor exponent takes the form: \(-2\pi^2[h^2a^2U_{11}+...+2hka`b`U_{12}]\).
Table A.36. Hydrogen atomic coordinates and isotropic atomic displacement parameters for N-pentafluorosulfanyl-1,3-dioxolan-2-imine (Compound 5).

<table>
<thead>
<tr>
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<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq) (Å²)</th>
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<tr>
<td>H3A</td>
<td>-0.3725</td>
<td>0.1936</td>
<td>-0.5089</td>
<td>0.017</td>
</tr>
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<td>H3B</td>
<td>-0.3938</td>
<td>0.1019</td>
<td>-0.3729</td>
<td>0.017</td>
</tr>
<tr>
<td>H2A</td>
<td>-0.2048</td>
<td>0.0433</td>
<td>-0.5915</td>
<td>0.016</td>
</tr>
<tr>
<td>H2B</td>
<td>-0.1273</td>
<td>0.1409</td>
<td>-0.6444</td>
<td>0.016</td>
</tr>
</tbody>
</table>
Figure A. 2.6. $^1$H NMR spectrum of 2-difluoro(pentafluorosulfanyl)acetylamino-5-methylbenzamide (Compound 6).
Figure A. $^{19}\text{F}$ NMR spectrum of 2-difluoro(pentafluorosulfanyl)acetylamino-5-methylbenzamide (Compound 6).
Figure A.28. IR spectrum of 2-difluoro(pentafluorosulfanyl)acetylaminoo-5-methylbenzamide (Compound 6).
Figure A. 29. $^1$H NMR spectrum of 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).
Figure A.30. $^{19}$F NMR spectrum of 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).
Figure A. 13C NMR spectrum of 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).
Figure A.32. HRMS of 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).
Figure A.33. IR spectrum of 2-(difluoro-(pentfluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).
Figure A.34. ORTEP (a), packing structure (b), H···O and H···F contacts (c), and F···F contact in the crystal structure of 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).
Table A. 37. Sample and crystal data for 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).

<table>
<thead>
<tr>
<th>Identification code</th>
<th>2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone</th>
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</thead>
<tbody>
<tr>
<td>Chemical formula</td>
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<tr>
<td>Formula weight</td>
<td>336.24 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.024x0.024x0.412 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_{1}/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
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</tr>
<tr>
<td>Volume</td>
<td>1160.8(2) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.924 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.373 mm(^{-1})</td>
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<td>F(000)</td>
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</tr>
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</table>

Table A.38. Data collection and structure refinement for 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).

| Theta range for data collection | 2.15° to 25.24° |
| Index ranges                   | -13<=h<=13, -6<=k<=6, -23<=l<=23 |
| Reflections collected          | 17051                               |
| Independent reflections        | 1942 \([R_{int}= 0.0580]\)         |
| Max. and min. transmission     | 1.0000 and 0.9395                    |
| Structure solution technique   | direct methods                      |
| Structure solution program     | SHELXT-2014 (Sheldrick 2014)        |
| Refinement method              | Full-matrix least-squares on F²    |
| Refinement program             | SHELXL-2014 (Sheldrick 2014)        |
| Function minimized             | \(\Sigma w(F_o^2-F_c^2)^2\)        |
| Data / restraints / parameters | 1942 / 0 / 191                       |
| Goodness-of-fit on F²          | 1.183                               |
| Final R indices                | 1628 data; I>2σ(I) R1= 0.0503, wR2= 0.1438 |
|                               | all data R1= 0.0644, wR2= 0.1688 |
| Weighting scheme              | \(w=1/[σ^2(F_o^2)+(0.0837P)^2+3.1185P]\) |
|                               | where P=(F_o^2+2F_c^2)/3            |
| Largest diff. peak and hole    | 0.558 and -0.875 eÅ³                |
| R.M.S. deviation from mean     | 0.188 eÅ³                            |
Table A.39. Atomic coordinates and equivalent isotropic atomic displacement parameters for 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).

<table>
<thead>
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<th>y/b</th>
<th>z/c</th>
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</thead>
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<td>0.8323(9)</td>
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</tr>
<tr>
<td>F1</td>
<td>0.9409(19)</td>
<td>0.0670(4)</td>
<td>0.5778(12)</td>
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<tr>
<td>F2</td>
<td>0.7732(2)</td>
<td>0.2414(4)</td>
<td>0.5814(12)</td>
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<tr>
<td>F3</td>
<td>0.8382(2)</td>
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<td>F4</td>
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<td>0.6795(5)</td>
<td>0.6507(14)</td>
<td>0.0445(8)</td>
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<tr>
<td>F5</td>
<td>0.7208(3)</td>
<td>0.0523(6)</td>
<td>0.6866(16)</td>
<td>0.0492(9)</td>
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<tr>
<td>F6</td>
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<td>0.7307(8)</td>
<td>0.6686(18)</td>
<td>0.0725(14)</td>
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<tr>
<td>F7</td>
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<td>0.7061(15)</td>
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*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.
Table A.40. Bond lengths for 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).

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<td>S1-F5</td>
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</tr>
<tr>
<td>S1-F6</td>
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<td>S1-F3</td>
<td>1.556(3)</td>
</tr>
<tr>
<td>S1-F4</td>
<td>1.564(3)</td>
<td>S1-C10</td>
<td>1.893(4)</td>
</tr>
<tr>
<td>F1-C10</td>
<td>1.324(4)</td>
<td>F2-C10</td>
<td>1.332(4)</td>
</tr>
<tr>
<td>O1-C2</td>
<td>1.222(5)</td>
<td>N1-C1</td>
<td>1.277(5)</td>
</tr>
<tr>
<td>N1-C4</td>
<td>1.383(5)</td>
<td>N2-C1</td>
<td>1.358(5)</td>
</tr>
<tr>
<td>N2-C2</td>
<td>1.366(5)</td>
<td>N2-H2</td>
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</tr>
<tr>
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<td>C2-C3</td>
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</tr>
<tr>
<td>C3-C8</td>
<td>1.389(5)</td>
<td>C3-C4</td>
<td>1.399(5)</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.393(5)</td>
<td>C5-C6</td>
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</tr>
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<td>C6-C7</td>
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<td>C7-C8</td>
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Table A.41. Bond angles for 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).

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<tr>
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<td>F4-S1-C10</td>
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</tr>
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<td>C3-C8-H8</td>
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<tr>
<td>C7-C9-H9B</td>
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</tr>
<tr>
<td>C7-C9-H9C</td>
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<tr>
<td>H9B-C9-H9C</td>
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N/A
Table A.42. Anisotropic atomic displacement parameters for 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).

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<th>$U_{22}$ (Å$^2$)</th>
<th>$U_{33}$ (Å$^2$)</th>
<th>$U_{23}$ (Å$^2$)</th>
<th>$U_{13}$ (Å$^2$)</th>
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<tr>
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<td>0.0244(12)</td>
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<td>0.0033(9)</td>
</tr>
<tr>
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<td>0.0111(13)</td>
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<tr>
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<td>0.0328(16)</td>
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<td>0.056(2)</td>
<td>0.0296(17)</td>
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<td>0.0286(16)</td>
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<td>-0.0029(11)</td>
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<td>0.0141(18)</td>
<td>0.0018(15)</td>
<td>0.0023(15)</td>
<td>0.0026(15)</td>
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<td>0.0027(15)</td>
<td>0.0028(14)</td>
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<tr>
<td>C5</td>
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<td>0.0031(15)</td>
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<td>0.016(2)</td>
<td>0.0173(19)</td>
<td>0.0000(16)</td>
<td>0.0034(15)</td>
<td>0.0023(16)</td>
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</tbody>
</table>

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2a^2U_{11} + \ldots + 2hka'b'U_{12}]$. 

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Table A.43. Hydrogen atomic coordinates and isotropic atomic displacement parameters for 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq) (Å²)</th>
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<tr>
<td>H2</td>
<td>0.6158</td>
<td>0.9942</td>
<td>0.5292</td>
<td>0.018</td>
</tr>
<tr>
<td>H5</td>
<td>0.9276</td>
<td>0.3488</td>
<td>0.4343</td>
<td>0.021</td>
</tr>
<tr>
<td>H6</td>
<td>0.8334</td>
<td>0.0746</td>
<td>0.3511</td>
<td>0.023</td>
</tr>
<tr>
<td>H8</td>
<td>0.5165</td>
<td>0.3780</td>
<td>0.3659</td>
<td>0.019</td>
</tr>
<tr>
<td>H9A</td>
<td>0.5201</td>
<td>0.0194</td>
<td>0.2949</td>
<td>0.031</td>
</tr>
<tr>
<td>H9B</td>
<td>0.6382</td>
<td>-0.1461</td>
<td>0.3040</td>
<td>0.031</td>
</tr>
<tr>
<td>H9C</td>
<td>0.6199</td>
<td>0.0768</td>
<td>0.2478</td>
<td>0.031</td>
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Table A.44. Hydrogen bond distances and angles for 2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone (Compound Q1).

<table>
<thead>
<tr>
<th></th>
<th>Donor-H (Å)</th>
<th>Acceptor-H (Å)</th>
<th>Donor-Acceptor (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-H2-O1</td>
<td>0.88</td>
<td>1.87</td>
<td>2.742(4)</td>
<td>169.8</td>
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</table>
Figure A. 35. $^1$H NMR spectrum of 5-chloro-2-[(2,2-difluoro-2-pentafluorosulfanyl-acetyl)amino]-benzamide (Compound 7).
Figure A.36. $^{19}F$ NMR spectrum of 5-chloro-2-(2,2-difluoro-2-pentafluorosulfonyl)acetylamino)-benzamide (Compound 7).
Figure A.37. $^{13}$C NMR spectrum of 5-chloro-2-[(2,2-difluoro-2-pentafluorosulfanyl-acetyl)amino]-benzamide (Compound 7).
Figure A.38: IR spectrum of 5-chloro-2-(2,2-difluoro-2-pentafluorosulfanyl-acetyl)amino-benzamide (Compound 7).
Figure A. 39. $^1$H NMR spectrum of 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3$H$)-one (Compound Q2).
Figure A.40. $^{19}$F NMR spectrum of 6-chloro-2-(difluoro(pentafluorosulfanyl)methyl)quinazolin-4(3H)-one (Compound Q2).
Figure A. 13C NMR spectrum of 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).
Figure A.42. HRMS of 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).
Figure A.43. IR spectrum of 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).
Figure A.44. ORTEP (a), packing structure (b), H···O contacts (c), and F···F contact in the crystal structure of 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).
Table A.45. Sample and crystal data for 6-chloro-2-
[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).

<table>
<thead>
<tr>
<th>Identification code</th>
<th>6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one</th>
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</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₉H₄ClF₇N₂OS</td>
</tr>
<tr>
<td>Formula weight</td>
<td>356.65 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>140(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.031x0.042x0.309 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2₁/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a= 11.4791(11) Å, b= 5.4243(6) Å, c= 19.218(2) Å, β= 99.237(3)°</td>
</tr>
<tr>
<td>Volume</td>
<td>1181.1(2) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>2.006 g/cm³</td>
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<tr>
<td>Absorption coefficient</td>
<td>0.592 mm⁻¹</td>
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<tr>
<td>F(000)</td>
<td>704</td>
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Table A.46. Data collection and structure refinement for 6-chloro-2-
[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).

<table>
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<tr>
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</thead>
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<td>Reflections collected</td>
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</tr>
<tr>
<td>Independent reflections</td>
<td>2325 [R_{int}= 0.0473]</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.0000 and 0.9395</td>
</tr>
<tr>
<td>Structure solution technique</td>
<td>direct methods</td>
</tr>
<tr>
<td>Structure solution program</td>
<td>SHELXT-2014 (Sheldrick 2014)</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Refinement program</td>
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<tr>
<td>Function minimized</td>
<td>Σw(Fo²-Fc²)²</td>
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<tr>
<td>Data / restraints / parameters</td>
<td>2325 / 28 / 227</td>
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<tr>
<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices</td>
<td>1987 data; I&gt;2σ(I) R1= 0.0391, wR2= 0.0947</td>
</tr>
<tr>
<td></td>
<td>all data R1= 0.0487, wR2= 0.0998</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>w=1/[o²(Fo²)+(0.0461P)²+1.9011P] where P=(Fo²+2Fc²)/3</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.479 and -0.445 eÅ⁻³</td>
</tr>
<tr>
<td>R.M.S. deviation from mean</td>
<td>0.068 eÅ⁻³</td>
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Table A.47. Atomic coordinates and equivalent isotropic atomic displacement parameters for 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).

<table>
<thead>
<tr>
<th></th>
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<th>y/b</th>
<th>z/c</th>
<th>U(eq) (Å²)</th>
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<tr>
<td>S1</td>
<td>0.1692(6)</td>
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<td>0.02419(18)</td>
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<tr>
<td>Cl</td>
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<td>0.0028(13)</td>
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<td>0.03037(19)</td>
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<tr>
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<td>0.7588(3)</td>
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<td>0.0259(4)</td>
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<td>0.0261(4)</td>
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<td>0.0482(5)</td>
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<td>0.3130(5)</td>
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<td>0.0421(8)</td>
</tr>
<tr>
<td>F5</td>
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<td>0.9393(6)</td>
<td>0.3129(18)</td>
<td>0.0541(9)</td>
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<tr>
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<td>0.2934(16)</td>
<td>0.0810(14)</td>
</tr>
<tr>
<td>F4B</td>
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<td>0.362(2)</td>
<td>0.3452(9)</td>
<td>0.0426(14)</td>
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<tr>
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<td>0.017(5)</td>
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<tr>
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<td>0.0182(4)</td>
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<td>0.5493(12)</td>
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<tr>
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<td>0.5799(13)</td>
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<tr>
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<tr>
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<td>0.9767(5)</td>
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<td>0.0188(5)</td>
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Table A.48. Bond lengths for 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).

<table>
<thead>
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<th>Bond length (Å)</th>
<th>Bond</th>
<th>Bond length (Å)</th>
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<td>S1-F4B</td>
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<td>S1-F5B</td>
<td>1.536(10)</td>
</tr>
<tr>
<td>S1-F7B</td>
<td>1.545(10)</td>
<td>S1-F7</td>
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</tr>
<tr>
<td>S1-F5</td>
<td>1.557(2)</td>
<td>S1-F6B</td>
<td>1.560(9)</td>
</tr>
<tr>
<td>S1-F3</td>
<td>1.5606(17)</td>
<td>S1-F6</td>
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<tr>
<td>S1-F4</td>
<td>1.583(2)</td>
<td>S1-C9</td>
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</tr>
<tr>
<td>Cl1-C7</td>
<td>1.735(3)</td>
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<td>N1-C4</td>
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<tr>
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<td>C4-C5</td>
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<td>C5-C6</td>
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<tr>
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Table A.49. Bond angles (°) for 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).

<table>
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<tr>
<th>Bonding Atoms</th>
<th>Bond angle (°)</th>
<th>Bonding Atoms</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
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<td>175.4(13)</td>
</tr>
<tr>
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<td>F7-S1-F5</td>
<td>91.84(19)</td>
</tr>
<tr>
<td>F4B-S1-F6B</td>
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<td>F5B-S1-F6B</td>
<td>169.8(14)</td>
</tr>
<tr>
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<tr>
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<tr>
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<td>F5-S1-F3</td>
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<tr>
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<td>89.65(12)</td>
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<td>87.52(15)</td>
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<tr>
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<tr>
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<td>C1-N1-C4</td>
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<td>C1-N2-H2</td>
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<td>119.2</td>
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</tr>
<tr>
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<td>O1-C2-C3</td>
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</tr>
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<td>C8-C3-C4</td>
<td>121.0(2)</td>
</tr>
<tr>
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<td>C4-C3-C2</td>
<td>119.1(2)</td>
</tr>
<tr>
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<td>N1-C4-C5</td>
<td>118.9(2)</td>
</tr>
<tr>
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<td>C6-C5-C4</td>
<td>120.1(2)</td>
</tr>
<tr>
<td>C6-C5-H5</td>
<td>119.9</td>
<td>C4-C5-H5</td>
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<td>C8-C7-C6</td>
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</tr>
<tr>
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<td>119.23(19)</td>
<td>C6-C7-C11</td>
<td>119.37(19)</td>
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<td>C7-C8-H8</td>
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<tr>
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<td>107.8(2)</td>
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<td>F1-C9-C1</td>
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</tr>
<tr>
<td>F2-C9-S1</td>
<td>106.75(15)</td>
<td>F1-C9-S1</td>
<td>106.34(16)</td>
</tr>
<tr>
<td>C1-C9-S1</td>
<td>113.90(17)</td>
<td>N/A</td>
<td>N/A</td>
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</table>
Table A.50. Anisotropic atomic displacement parameters (Å\(^2\)) for 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).

<table>
<thead>
<tr>
<th></th>
<th>(U_{11}) (Å(^2))</th>
<th>(U_{22}) (Å(^2))</th>
<th>(U_{33}) (Å(^2))</th>
<th>(U_{12}) (Å(^2))</th>
<th>(U_{13}) (Å(^2))</th>
<th>(U_{23}) (Å(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0210(3)</td>
<td>0.0318(4)</td>
<td>0.0192(3)</td>
<td>-0.0002(3)</td>
<td>0.0018(2)</td>
<td>-0.0015(3)</td>
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<tr>
<td>Cl1</td>
<td>0.0317(4)</td>
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<td>0.0299(3)</td>
<td>-0.0115(3)</td>
<td>0.0009(3)</td>
<td>0.0029(3)</td>
</tr>
<tr>
<td>F1</td>
<td>0.0276(8)</td>
<td>0.0164(7)</td>
<td>0.0323(8)</td>
<td>-0.0013(6)</td>
<td>0.0005(6)</td>
<td>0.0044(6)</td>
</tr>
<tr>
<td>F2</td>
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<td>0.0308(8)</td>
<td>-0.0015(7)</td>
<td>0.0060(6)</td>
<td>-0.0061(6)</td>
</tr>
<tr>
<td>F3</td>
<td>0.0485(11)</td>
<td>0.0738(14)</td>
<td>0.0215(8)</td>
<td>0.0102(9)</td>
<td>0.0026(7)</td>
<td>0.0111(10)</td>
</tr>
<tr>
<td>F4</td>
<td>0.064(2)</td>
<td>0.0352(12)</td>
<td>0.0280(10)</td>
<td>-0.0007(9)</td>
<td>0.0094(12)</td>
<td>0.0229(13)</td>
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<tr>
<td>F5</td>
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<td>0.052(2)</td>
<td>0.052(2)</td>
<td>0.0039(14)</td>
<td>0.0388(13)</td>
<td>0.0280(14)</td>
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<tr>
<td>F6</td>
<td>0.0507(15)</td>
<td>0.096(3)</td>
<td>0.0559(17)</td>
<td>0.0471(18)</td>
<td>0.0251(13)</td>
<td>0.0503(18)</td>
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<tr>
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<td>0.118(3)</td>
<td>0.0260(11)</td>
<td>0.0079(14)</td>
<td>0.0053(18)</td>
<td>-0.086(2)</td>
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<td>F4B</td>
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<td>0.035(2)</td>
<td>0.053(3)</td>
<td>0.005(3)</td>
<td>0.038(2)</td>
<td>0.027(2)</td>
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<tr>
<td>F5B</td>
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<td>0.053(3)</td>
<td>0.053(3)</td>
<td>0.005(3)</td>
<td>0.038(2)</td>
<td>0.027(2)</td>
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<tr>
<td>F6B</td>
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<td>0.095(4)</td>
<td>0.055(3)</td>
<td>0.047(3)</td>
<td>0.024(2)</td>
<td>0.051(3)</td>
</tr>
<tr>
<td>F7B</td>
<td>0.095(4)</td>
<td>0.116(3)</td>
<td>0.026(2)</td>
<td>-0.008(2)</td>
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<tr>
<td>O1</td>
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<td>0.0017(8)</td>
<td>0.0072(8)</td>
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<tr>
<td>C1</td>
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<td>0.0031(10)</td>
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<td>0.0011(9)</td>
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<td>0.0209(12)</td>
<td>0.0005(10)</td>
<td>0.0018(9)</td>
<td>0.0034(10)</td>
</tr>
<tr>
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<td>0.0187(11)</td>
<td>0.0002(10)</td>
<td>0.0033(9)</td>
<td>0.0049(10)</td>
</tr>
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<td>0.0040(9)</td>
<td>0.0034(10)</td>
</tr>
<tr>
<td>C5</td>
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<td>0.0251(13)</td>
<td>0.0016(11)</td>
<td>0.0056(10)</td>
<td>0.0077(11)</td>
</tr>
<tr>
<td>C6</td>
<td>0.0237(14)</td>
<td>0.0252(14)</td>
<td>0.0235(13)</td>
<td>0.0037(11)</td>
<td>0.0074(10)</td>
<td>0.0099(11)</td>
</tr>
<tr>
<td>C7</td>
<td>0.0244(13)</td>
<td>0.0192(13)</td>
<td>0.0183(12)</td>
<td>0.0012(10)</td>
<td>0.0027(10)</td>
<td>0.0030(10)</td>
</tr>
<tr>
<td>C8</td>
<td>0.0180(12)</td>
<td>0.0202(13)</td>
<td>0.0218(12)</td>
<td>0.0007(10)</td>
<td>0.0006(9)</td>
<td>0.0025(10)</td>
</tr>
<tr>
<td>C9</td>
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<td>0.0189(13)</td>
<td>0.0239(12)</td>
<td>0.0011(10)</td>
<td>0.0032(9)</td>
<td>0.0025(10)</td>
</tr>
</tbody>
</table>

The anisotropic atomic displacement factor exponent takes the form: \(-2\pi^2[h^2a^2U_{11} + ... + 2hka'b'U_{12}].\)
Table A.51. Hydrogen atomic coordinates and isotropic atomic displacement parameters for 6-chloro-2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q2).

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.4706</td>
<td>0.023</td>
</tr>
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<td>H5</td>
<td>0.0723</td>
<td>0.6477</td>
<td>0.5666</td>
<td>0.028</td>
</tr>
<tr>
<td>H6</td>
<td>0.1668</td>
<td>0.9224</td>
<td>0.6496</td>
<td>0.028</td>
</tr>
<tr>
<td>H8</td>
<td>0.4844</td>
<td>0.6180</td>
<td>0.6338</td>
<td>0.024</td>
</tr>
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</table>
Figure A.45. $^1$H NMR spectrum of 6-[[difluoro(pentafluorosulfanyl)acetyl]amino]-1,3-benzodioxole-5-carboxamide (Compound 8).
Figure A.46. $^{19}$F NMR spectrum of 6-[(difluoro(pentafluorosulfanyl)acetyl)amino]-1,3-benzodioxole-5-carboxamide (Compound 8).
Figure A.47. IR spectrum of 6-[(difluoro(pentafluorosulfanyl)acetyl)amino]-1,3-benzodioxole-5-carboxamide (Compound 8).
Figure A.48. $^1$H NMR spectrum of 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).
Figure A.49. $^{19}$F NMR spectrum of 6-[difluoro(pentafluorosulfanyl)methyl][1,3]dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).
Figure A. 50. $^{13}$C NMR spectrum of 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).
Figure A.51. IR spectrum of 6-{difluoro(pentafluorosulfanyl)methyl}[1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).
Figure A.52. ORTEP (a), packing structure (b), F···F contacts (c), and H-bonding (d) in the crystal structure of 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5]-quinazolin-8(7H)-one (Compound Q3).

Table A.52. Sample and crystal data for 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).

<table>
<thead>
<tr>
<th>Identification code</th>
<th>6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one</th>
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<tr>
<td>Chemical formula</td>
<td>C_{10}H_{5}F_{7}N_{2}O_{3}S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>366.22 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>140(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>-----------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.045x0.092x0.314 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P̅1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>(a= 5.3789(4) \text{ Å}) (\alpha= 76.678(4)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(b= 10.4131(9) \text{ Å}) (\beta= 83.081(3)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c= 11.1484(10) \text{ Å}) (\gamma= 78.317(3)^\circ)</td>
</tr>
<tr>
<td>Volume</td>
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</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
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<td>Absorption coefficient</td>
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<td>F(000)</td>
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Table A.53. Data collection and structure refinement for 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).

| Theta range for data collection | 3.06° to 25.50° |
| Index ranges                  | -6<=h<=6, -12<=k<=12, -13<=l<=13 |
| Reflections collected         | 14795 |
| Independent reflections       | 2205 \([R_{int}= 0.0347]\) |
| Max. and min. transmission    | 1.0000 and 0.9329 |
| Structure solution technique  | direct methods |
| Structure solution program    | SHELXT-2014 (Sheldrick 2014) |
| Refinement method             | Full-matrix least-squares on \(F^2\) |
| Refinement program            | SHELXL-2014 (Sheldrick 2014) |
| Function minimized            | \(\Sigma w(F_o^2-F_c^2)^2\) |
| Data / restraints / parameters| 2205 / 1 / 212 |
| Goodness-of-fit on \(F^2\)    | 1.143 |
| Final R indices               | \(R(1)= 0.0497, wR(2)= 0.1285\) |
|                               | all data \(R(1)= 0.0553, wR(2)= 0.1320\) |
| Weighting scheme              | \(w=1/[\sigma^2(F_o^2)+(0.0529P)^2+1.3154P]\) where \(P=(F_o^2+2F_c^2)/3\) |
| Largest diff. peak and hole   | 0.522 eÅ⁻³ and -0.509 eÅ⁻³ |
| R.M.S. deviation from mean    | 0.085 eÅ⁻³ |

Table A.54. Atomic coordinates and equivalent isotropic atomic displacement parameters for 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).

<table>
<thead>
<tr>
<th></th>
<th>(x/a)</th>
<th>(y/b)</th>
<th>(z/c)</th>
<th>(U(eq)) (Å²)</th>
</tr>
</thead>
<tbody>
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<td>S1</td>
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<td>0.84120(8)</td>
<td>0.0259(2)</td>
</tr>
<tr>
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<td>0.0305(5)</td>
</tr>
<tr>
<td>F2</td>
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<td>0.81247(19)</td>
<td>0.0292(5)</td>
</tr>
<tr>
<td></td>
<td>Bond lengths (Å)</td>
<td></td>
<td>Bond lengths (Å)</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>-----------------</td>
<td>----</td>
<td>-----------------</td>
<td></td>
</tr>
<tr>
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<td>0.9773(5)</td>
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</tr>
<tr>
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<td>0.0202(2)</td>
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</tr>
<tr>
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<td>0.4556(4)</td>
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<td></td>
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<td></td>
<td>0.2198(3)</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>O4</td>
<td>0.8529(4)</td>
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<tr>
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<td>0.6653(3)</td>
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</table>

Table A.55. Bond lengths for 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).
Table A.56. Bond angles for 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).

<table>
<thead>
<tr>
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<th>Bond angle (°)</th>
<th>Bonding Atoms</th>
<th>Bond angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F6-S1-F4</td>
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<td>89.34(14)</td>
</tr>
<tr>
<td>F4-S1-F3</td>
<td>88.78(14)</td>
<td>F6-S1-F7</td>
<td>90.19(15)</td>
</tr>
<tr>
<td>F4-S1-F7</td>
<td>176.71(14)</td>
<td>F3-S1-F7</td>
<td>88.67(12)</td>
</tr>
<tr>
<td>F6-S1-F5</td>
<td>176.78(13)</td>
<td>F4-S1-F5</td>
<td>89.85(15)</td>
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</table>
Table A.57. Anisotropic atomic displacement parameters for:
6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).

<table>
<thead>
<tr>
<th></th>
<th>U_{11} (Å^2)</th>
<th>U_{22} (Å^2)</th>
<th>U_{33} (Å^2)</th>
<th>U_{12} (Å^2)</th>
<th>U_{13} (Å^2)</th>
<th>U_{23} (Å^2)</th>
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</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0272(4)</td>
<td>0.0220(4)</td>
<td>0.0264(5)</td>
<td>-0.0014(3)</td>
<td>-0.0026(3)</td>
<td>-0.0037(3)</td>
</tr>
<tr>
<td>F1</td>
<td>0.0396(11)</td>
<td>0.0357(11)</td>
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<td>-0.0079(8)</td>
<td>0.0073(8)</td>
<td>-0.0156(9)</td>
</tr>
<tr>
<td>F2</td>
<td>0.0170(9)</td>
<td>0.0297(11)</td>
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<td>-0.0023(9)</td>
<td>-0.0049(8)</td>
<td>-0.0102(8)</td>
</tr>
<tr>
<td>F3</td>
<td>0.0538(15)</td>
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<td>0.0620(16)</td>
<td>0.0025(10)</td>
<td>0.0015(12)</td>
<td>0.0027(10)</td>
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</tbody>
</table>
The anisotropic atomic displacement factor exponent takes the form: 
\[ -2\pi^2[\hat{h}^2 a^2 U_{11} + \ldots + 2hk\alpha b^2 U_{12}] \].

Table A.58. Hydrogen atomic coordinates and isotropic atomic displacement parameters for 6-[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one (Compound Q3).

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.024(6)</td>
<td>0.451(3)</td>
<td>0.626(3)</td>
<td>0.024(9)</td>
</tr>
<tr>
<td>H5</td>
<td>0.5921</td>
<td>0.6394</td>
<td>0.9043</td>
<td>0.023</td>
</tr>
<tr>
<td>H8</td>
<td>0.5093</td>
<td>0.7743</td>
<td>0.4701</td>
<td>0.023</td>
</tr>
</tbody>
</table>
Table A.59. Hydrogen bond distances and angles for 6-
[difluoro(pentafluorosulfanyl)methyl][1,3] dioxolo [4,5] quinazolin-8(7H)-one
(Compound Q3).

<table>
<thead>
<tr>
<th></th>
<th>Donor-H (Å)</th>
<th>Acceptor-H (Å)</th>
<th>Donor-Acceptor (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2-H2–O1</td>
<td>0.850(19)</td>
<td>1.96(2)</td>
<td>2.802(3)</td>
<td>170.3(3)</td>
</tr>
<tr>
<td>C8-H8–F7</td>
<td>0.95</td>
<td>2.62</td>
<td>3.544(4)</td>
<td>163.2</td>
</tr>
<tr>
<td>C9-H9B–F5</td>
<td>0.99</td>
<td>2.57</td>
<td>3.169(4)</td>
<td>118.8</td>
</tr>
</tbody>
</table>
Figure A.53. $^1$H NMR spectrum of 2[2,2-difluoro(pentafluorosulfanyl)acetamide] benzamide (Compound 9).
Figure A.54. $^{19}$F NMR spectrum of 2[2,2-difluoro(pentafluorosulfanyl)acetamide] benzamide (Compound 9).
Figure A.55. $^{13}$C NMR spectrum of 2[2,2-difluoro(pentafluorosulfanyl)acetamide] benzamide (Compound 9).
Figure A.56. $^1$H NMR spectrum of 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).
Figure A.57. $^{19}$F NMR spectrum of 2-[difluoro(pentafluorosulfanyl)methyl]quinazolin-4(3H)-one (Compound Q4).
Figure A.58. $^{13}$C NMR spectrum of 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).
Figure A.59. ORTEP (a), packing structure (b), F···F contacts (c), H···O contact (d), and H···F contact (e) in the crystal structure of 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).

Table A.60. Sample and crystal data for 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).
<table>
<thead>
<tr>
<th>Identification code</th>
<th>2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₉H₅F₇N₂SO</td>
</tr>
<tr>
<td>Formula weight</td>
<td>322.21 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.056x0.176x0.571 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$\overline{P}$</td>
</tr>
<tr>
<td>a</td>
<td>5.3316(3) Å</td>
</tr>
<tr>
<td>α</td>
<td>85.041(2)°</td>
</tr>
<tr>
<td>b</td>
<td>9.6257(6) Å</td>
</tr>
<tr>
<td>β</td>
<td>82.648(2)°</td>
</tr>
<tr>
<td>c</td>
<td>10.9910(6) Å</td>
</tr>
<tr>
<td>γ</td>
<td>85.965(2)°</td>
</tr>
<tr>
<td>Volume</td>
<td>556.33(6) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.923 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.385 mm⁻¹</td>
</tr>
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<td>F(000)</td>
<td>320</td>
</tr>
</tbody>
</table>

Table A.61. Data collection and structure refinement for 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).

| Theta range for data collection | 2.72° to 26.49° |
| Index ranges                   | -6<=$h$<=$6$, -12<=$k$<=$12$, -13<=$l$<=$13$ |
| Reflections collected          | 18024             |
| Independent reflections        | 2308 [R(int) = 0.0245] |
| Max. and min. transmission     | 1.0000 and 0.9262 |
| Structure solution technique   | direct methods    |
| Structure solution program     | SHELXT-2014 (Sheldrick 2014) |
| Refinement method              | Full-matrix least-squares on F² |
| Refinement program             | SHELXL-2014 (Sheldrick 2014) |
| Function minimized             | $\Sigma w(F_o^2-f_c^2)^2$ |
| Data / restraints / parameters | 2308 / 0 / 181 |
| Goodness-of-fit on F²          | 1.174             |
| Final R indices                | 2131 data; I>2σ(I); R1 = 0.0270, wR2 = 0.0811 |
|                               | all data R1 = 0.0324, wR2 = 0.0950 |
| Weighting scheme               | $w=1/[σ^2(F_o^2)+(0.0572P)^2+0.2164P]$ where P = (F_o^2+2F_c^2)/3 |
| Largest diff. peak and hole    | 0.500 eÅ⁻³ and -0.620 eÅ⁻³ |
| R.M.S. deviation from mean     | 0.189 eÅ⁻³ |

Table A.62. Atomic coordinates and equivalent isotropic atomic displacement parameters for 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).
Table A.63. Bond lengths for 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond lengths (Å)</th>
<th>Bond</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-F4</td>
<td>1.5678(10)</td>
<td>S1-F7</td>
<td>1.5725(11)</td>
</tr>
<tr>
<td>S1-F3</td>
<td>1.5798(9)</td>
<td>S1-F5</td>
<td>1.5823(10)</td>
</tr>
<tr>
<td>S1-F6</td>
<td>1.5826(10)</td>
<td>S1-C1</td>
<td>1.9087(16)</td>
</tr>
</tbody>
</table>
Table A.64. Bond angles for
2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).

<table>
<thead>
<tr>
<th>Bonding Atoms</th>
<th>Bond Angle (°)</th>
<th>Bonding Atoms</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F4-S1-F7</td>
<td>89.18(6)</td>
<td>F4-S1-F3</td>
<td>89.05(6)</td>
</tr>
<tr>
<td>F7-S1-F3</td>
<td>89.68(5)</td>
<td>F4-S1-F5</td>
<td>88.89(6)</td>
</tr>
<tr>
<td>F7-S1-F5</td>
<td>91.01(6)</td>
<td>F3-S1-F5</td>
<td>177.82(6)</td>
</tr>
<tr>
<td>F4-S1-F6</td>
<td>88.79(6)</td>
<td>F7-S1-F6</td>
<td>177.51(6)</td>
</tr>
<tr>
<td>F3-S1-F6</td>
<td>88.85(5)</td>
<td>F5-S1-F6</td>
<td>90.38(6)</td>
</tr>
<tr>
<td>F4-S1-C1</td>
<td>177.58(6)</td>
<td>F7-S1-C1</td>
<td>90.75(6)</td>
</tr>
<tr>
<td>F3-S1-C1</td>
<td>93.37(6)</td>
<td>F5-S1-C1</td>
<td>88.69(6)</td>
</tr>
<tr>
<td>F6-S1-C1</td>
<td>91.34(6)</td>
<td>C2-N2-C5</td>
<td>115.96(13)</td>
</tr>
<tr>
<td>C2-N1-C3</td>
<td>121.52(13)</td>
<td>C2-N1-H1</td>
<td>119.2</td>
</tr>
<tr>
<td>C3-N1-H1</td>
<td>119.2</td>
<td>N2-C5-C6</td>
<td>118.54(13)</td>
</tr>
<tr>
<td>N2-C5-C4</td>
<td>122.07(13)</td>
<td>C6-C5-C4</td>
<td>119.38(14)</td>
</tr>
<tr>
<td>C7-C6-C5</td>
<td>119.57(14)</td>
<td>C7-C6-H6</td>
<td>120.2</td>
</tr>
<tr>
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<td>120.2</td>
<td>C9-C8-C7</td>
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</tr>
<tr>
<td>C9-C8-H8</td>
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<td>C7-C8-H8</td>
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<tr>
<td>C6-C7-C8</td>
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<td>C6-C7-H7</td>
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</tr>
<tr>
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<td>119.5</td>
<td>C9-C4-C5</td>
<td>120.37(14)</td>
</tr>
<tr>
<td>C9-C4-C3</td>
<td>120.44(14)</td>
<td>C5-C4-C3</td>
<td>119.19(14)</td>
</tr>
<tr>
<td>C8-C9-C4</td>
<td>119.64(14)</td>
<td>C8-C9-H9</td>
<td>120.2</td>
</tr>
<tr>
<td>C4-C9-H9</td>
<td>120.2</td>
<td>N2-C2-N1</td>
<td>126.85(14)</td>
</tr>
<tr>
<td>N2-C2-C1</td>
<td>117.44(13)</td>
<td>N1-C2-C1</td>
<td>115.70(13)</td>
</tr>
<tr>
<td>F1-C1-F2</td>
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<td>F1-C1-C2</td>
<td>110.99(12)</td>
</tr>
<tr>
<td>F2-C1-C2</td>
<td>110.67(12)</td>
<td>F1-C1-S1</td>
<td>106.69(10)</td>
</tr>
<tr>
<td>F2-C1-S1</td>
<td>105.86(10)</td>
<td>C2-C1-S1</td>
<td>114.14(10)</td>
</tr>
<tr>
<td>O1-C3-N1</td>
<td>121.22(14)</td>
<td>O1-C3-C4</td>
<td>124.37(14)</td>
</tr>
<tr>
<td>N1-C3-C4</td>
<td>114.40(13)</td>
<td>N/A</td>
<td>N/A</td>
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</table>

Table A.65. Torsion angles for
2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).
<table>
<thead>
<tr>
<th>Bonding Atoms</th>
<th>Torsion angle (°)</th>
<th>Bonding Atoms</th>
<th>Torsion angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2-N2-C5-C6</td>
<td>179.41(13)</td>
<td>C2-N2-C5-C4</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>N2-C5-C6-C7</td>
<td>-177.94(14)</td>
<td>C4-C5-C6-C7</td>
<td>0.6(2)</td>
</tr>
<tr>
<td>C5-C6-C7-C8</td>
<td>-0.5(2)</td>
<td>C9-C8-C7-C6</td>
<td>0.1(2)</td>
</tr>
<tr>
<td>N2-C5-C4-C9</td>
<td>178.31(14)</td>
<td>C6-C5-C4-C9</td>
<td>-0.2(2)</td>
</tr>
<tr>
<td>N2-C5-C4-C3</td>
<td>-1.3(2)</td>
<td>C6-C5-C4-C3</td>
<td>-179.77(13)</td>
</tr>
<tr>
<td>C7-C8-C9-C4</td>
<td>0.4(2)</td>
<td>C5-C4-C9-C8</td>
<td>-0.3(2)</td>
</tr>
<tr>
<td>C3-C4-C9-C8</td>
<td>179.28(14)</td>
<td>C5-N2-C2-N1</td>
<td>0.3(2)</td>
</tr>
<tr>
<td>C5-N2-C2-C1</td>
<td>-178.66(12)</td>
<td>C3-N1-C2-N2</td>
<td>-1.2(2)</td>
</tr>
<tr>
<td>C3-N1-C2-C1</td>
<td>177.82(13)</td>
<td>N2-C2-C1-F1</td>
<td>-27.12(19)</td>
</tr>
<tr>
<td>N1-C2-C1-F1</td>
<td>153.79(12)</td>
<td>N2-C2-C1-F2</td>
<td>-147.23(13)</td>
</tr>
<tr>
<td>N1-C2-C1-F2</td>
<td>33.68(18)</td>
<td>N2-C2-C1-S1</td>
<td>93.48(15)</td>
</tr>
<tr>
<td>N1-C2-C1-S1</td>
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<td>C2-N1-C3-O1</td>
<td>-179.30(13)</td>
</tr>
<tr>
<td>C2-N1-C3-C4</td>
<td>0.7(2)</td>
<td>C9-C4-C3-O1</td>
<td>0.8(2)</td>
</tr>
<tr>
<td>C5-C4-C3-O1</td>
<td>-179.56(14)</td>
<td>C9-C4-C3-N1</td>
<td>-179.16(14)</td>
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<tr>
<td>C5-C4-C3-N1</td>
<td>0.4(2)</td>
<td>N/A</td>
<td>N/A</td>
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Table A.66. Anisotropic atomic displacement parameters for 2-[ difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3$H$)-one (Compound Q4).
<table>
<thead>
<tr>
<th></th>
<th>U_{11} (Å²)</th>
<th>U_{22} (Å²)</th>
<th>U_{33} (Å²)</th>
<th>U_{23} (Å²)</th>
<th>U_{13} (Å²)</th>
<th>U_{12} (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.0131(2)</td>
<td>0.0102(2)</td>
<td>0.0167(2)</td>
<td>0.00046(15)</td>
<td>0.00157(16)</td>
<td>0.00248(15)</td>
</tr>
<tr>
<td>F1</td>
<td>0.0220(5)</td>
<td>0.0197(5)</td>
<td>0.0099(5)</td>
<td>-0.0021(4)</td>
<td>0.0034(4)</td>
<td>-0.0063(4)</td>
</tr>
<tr>
<td>F2</td>
<td>0.0083(4)</td>
<td>0.0179(5)</td>
<td>0.0240(5)</td>
<td>0.0016(4)</td>
<td>-0.0052(4)</td>
<td>-0.0028(3)</td>
</tr>
<tr>
<td>F3</td>
<td>0.0134(5)</td>
<td>0.0158(5)</td>
<td>0.0198(5)</td>
<td>-0.0029(4)</td>
<td>0.0028(4)</td>
<td>-0.0020(4)</td>
</tr>
<tr>
<td>F6</td>
<td>0.0233(5)</td>
<td>0.0257(5)</td>
<td>0.0246(6)</td>
<td>-0.0123(4)</td>
<td>-0.0082(4)</td>
<td>-0.0040(4)</td>
</tr>
<tr>
<td>F7</td>
<td>0.0224(5)</td>
<td>0.0310(6)</td>
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<td>0.0053(4)</td>
<td>-0.0090(4)</td>
<td>0.0043(4)</td>
</tr>
<tr>
<td>F4</td>
<td>0.0277(6)</td>
<td>0.0105(5)</td>
<td>0.0482(7)</td>
<td>-0.0018(5)</td>
<td>0.0033(5)</td>
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<tr>
<td>F5</td>
<td>0.0213(5)</td>
<td>0.0155(5)</td>
<td>0.0349(6)</td>
<td>0.0056(4)</td>
<td>0.0051(4)</td>
<td>-0.0070(4)</td>
</tr>
<tr>
<td>O1</td>
<td>0.0172(6)</td>
<td>0.0167(6)</td>
<td>0.0097(5)</td>
<td>0.0016(4)</td>
<td>-0.0052(4)</td>
<td>-0.0057(4)</td>
</tr>
<tr>
<td>N2</td>
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<td>0.0100(6)</td>
<td>-0.0015(5)</td>
<td>-0.0022(5)</td>
<td>-0.0003(5)</td>
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<tr>
<td>N1</td>
<td>0.0116(6)</td>
<td>0.0118(6)</td>
<td>0.0095(6)</td>
<td>-0.0012(5)</td>
<td>-0.0040(5)</td>
<td>-0.0028(5)</td>
</tr>
<tr>
<td>C5</td>
<td>0.0099(7)</td>
<td>0.0097(7)</td>
<td>0.0113(7)</td>
<td>-0.0023(6)</td>
<td>-0.0006(5)</td>
<td>-0.0001(5)</td>
</tr>
<tr>
<td>C6</td>
<td>0.0153(7)</td>
<td>0.0128(7)</td>
<td>0.0110(7)</td>
<td>-0.0020(6)</td>
<td>-0.0042(6)</td>
<td>-0.0004(6)</td>
</tr>
<tr>
<td>C8</td>
<td>0.0159(8)</td>
<td>0.0127(7)</td>
<td>0.0164(8)</td>
<td>-0.0010(6)</td>
<td>-0.0009(6)</td>
<td>-0.0055(6)</td>
</tr>
<tr>
<td>C7</td>
<td>0.0150(7)</td>
<td>0.0144(7)</td>
<td>0.0161(8)</td>
<td>-0.0052(6)</td>
<td>-0.0044(6)</td>
<td>-0.0032(6)</td>
</tr>
<tr>
<td>C4</td>
<td>0.0108(7)</td>
<td>0.0097(7)</td>
<td>0.0119(7)</td>
<td>-0.0024(6)</td>
<td>-0.0025(6)</td>
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</tr>
<tr>
<td>C9</td>
<td>0.0163(7)</td>
<td>0.0135(7)</td>
<td>0.0109(7)</td>
<td>0.0001(6)</td>
<td>-0.0012(6)</td>
<td>-0.0025(6)</td>
</tr>
<tr>
<td>C2</td>
<td>0.0094(7)</td>
<td>0.0087(7)</td>
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<td>-0.0013(5)</td>
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</tr>
<tr>
<td>C1</td>
<td>0.0097(7)</td>
<td>0.0125(7)</td>
<td>0.0107(7)</td>
<td>-0.0013(6)</td>
<td>-0.0018(5)</td>
<td>-0.0008(6)</td>
</tr>
<tr>
<td>C3</td>
<td>0.0112(7)</td>
<td>0.0106(7)</td>
<td>0.0119(7)</td>
<td>-0.0017(6)</td>
<td>-0.0013(6)</td>
<td>0.0004(5)</td>
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</table>

Table A.67. Hydrogen atomic coordinates and isotropic atomic displacement parameters for
2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).
Table A.68. Hydrogen bond distances and angles for 2-[difluoro(pentafluorosulfanyl)methyl] quinazolin-4(3H)-one (Compound Q4).

<table>
<thead>
<tr>
<th>Hydrogen Bond</th>
<th>Donor-H (Å)</th>
<th>Acceptor-H (Å)</th>
<th>Donor-Acceptor (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
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<td>N1-H1···O1</td>
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Figure A.60. $^1$H NMR spectrum of 3-[2,2-difluoro(pentafluorosulfanyl)acetamido]-thiophene-2-carboxamide (Compound 10).
Figure A.61. $^{19}$F NMR spectrum of 3-[(2,2-difluoropentafluorosulfanyl)acetamido]-thiophene-2-carboxamide (Compound 10).
Figure A.62. $^{13}$C NMR spectrum of 3-[2,2-difluoro(pentafluorosulfanyl)acetamido]-thiophene-2-carboxamide (Compound 10).
Figure A.63. ORTEP (a), packing structure (b), F···F contacts (c), H-bonding (d), H···F contacts (e), in the crystal structure of 2-[difluoro(pentafluorosulfanyl) methyl] thieno [3,2-\textit{d}] pyrimidin-4(3\textit{H})-one (Compound Q5).

Table A.69. Sample and crystal data for 2-[difluoro(pentafluorosulfanyl) methyl] thieno [3,2-\textit{d}] pyrimidin-4(3\textit{H})-one (Compound Q5).
Chemical formula | $\text{C}_7\text{H}_3\text{F}_7\text{N}_2\text{OS}_2$  
Formula weight | 328.23 g/mol  
Temperature | 100(2) K  
Wavelength | 0.71073 Å  
Crystal size | 0.041x0.046x0.422 mm  
Crystal system | monoclinic  
Space group | $P2_1/n$  
Unit cell dimensions | a= 5.5612(3) Å  
b= 9.8618(6) Å  
c= 19.0368(12) Å  
$\beta= 92.532(2)^\circ$  
Volume | 1043.02(11) Å$^3$  
Z | 4  
Density (calculated) | 2.090 g/cm$^3$  
Absorption coefficient | 0.605 mm$^{-1}$  
F(000) | 648

Table A.70. Data collection and structure refinement for
2-[difluoro(pentafluorosulfanyl) methyl] thieno [3,2-d] pyrimidin-4(3H)-one
(Compound Q5).

| Theta range for data collection | 2.14$^\circ$ to 26.00$^\circ$  
Index ranges | -6<=h<=6, -12<=k<=12, -23<=l<=23  
Reflections collected | 25114  
Independent reflections | 2043 [R(int) 0.0500]  
Max. and min. transmission | 1.0000 and 0.9396  
Structure solution technique | direct methods  
Structure solution program | SHELXT-2014 (Sheldrick 2014)  
Refinement method | Full-matrix least-squares on $F^2$  
Refinement program | SHELXL-2014 (Sheldrick 2014)  
Function minimized | $\Sigma w(F_o^2-F_c^2)^2$  
Data / restraints / parameters | 2043 / 0 / 172  
Goodness-of-fit on $F^2$ | 1.102  
Final R indices | 1750 data: $l>2\sigma(l)$ R1 = 0.0454, wR2 = 0.1143  
all data R1 = 0.0556, wR2 = 0.1198  
Weighting scheme | $w=1/\sigma^2(F_o^2)+(0.0518P)^2+2.3109P$  
where $P=(F_o^2+2F_c^2)/3$  
Largest diff. peak and hole | 0.593 eÅ$^3$ and -0.542 eÅ$^3$  
R.M.S. deviation from mean | 0.084 eÅ$^3$  

Table A.71. Atomic coordinates and equivalent isotropic atomic displacement parameters
for 2-[difluoro(pentafluorosulfanyl) methyl] thieno [3,2-d] pyrimidin-4(3H)-one
(Compound Q5).
<table>
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<th>y/b</th>
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<td>0.39836(5)</td>
<td>0.0333(3)</td>
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<td>0.46517(11)</td>
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Table A.72. Bond lengths for 2-[difluoro(pentafluorosulfanyl) methyl] thieno [3,2-d] pyrimidin-4(3H)-one (Compound Q5).
Table A.73. Bond lengths (Å) for 2-[difluoro(pentafluorosulfanyl) methyl] thieno [3,2-d] pyrimidin-4(3H)-one (Compound Q5).

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Table A.74. Anisotropic atomic displacement parameters for
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(Compound Q5).

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The anisotropic atomic displacement factor exponent takes the form: -2π²[a₁₁h² + ... + 2hka'b'U₁₂].

Table A.75. Hydrogen atomic coordinates and isotropic atomic displacement parameters for 2-[difluoro(pentafluorosulfanyl) methyl] thieno[3,2-d]pyrimidin-4(3H)-one (Compound Q5).

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254
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Figure A.64. $^1$H NMR spectrum of 3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide (Compound 11).
Figure A. 1H NMR spectrum of 3-difluoropentfluorosulfonylacetamidino-1-benzofuran-2-carboxamide (Compound 11).
Figure A.66. IR spectrum of 3-difluoro(pentafluorosulfonyl)acetylamino-1-benzofuran-2-carboxamide (Compound 11).
Figure A.67. ORTEP (a), packing structure (b), H-bonding (c), H···F contact (d), and F···F contact (e) of 3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide (Compound 11) crystal structure.
Table A.76. Sample and crystal data for 3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide (Compound 11).

<table>
<thead>
<tr>
<th>Identification code</th>
<th>3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide</th>
</tr>
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<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{11}H_{7}F_{7}N_{2}O_{3}S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>380.25 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.023x0.074x0.205 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a= 7.0109(10) Å</td>
</tr>
<tr>
<td></td>
<td>b= 9.2210(11) Å</td>
</tr>
<tr>
<td></td>
<td>c= 21.334(3) Å</td>
</tr>
<tr>
<td></td>
<td>β= 91.476(5)°</td>
</tr>
<tr>
<td>Volume</td>
<td>1378.7(3) Å</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.832 g/cm³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
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</tr>
<tr>
<td>F(000)</td>
<td>760</td>
</tr>
</tbody>
</table>

Table A.77. Data collection and structure refinement for 3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide (Compound 11).

| Theta range for data collection | 1.91° to 27.48° |
| Reflections collected           | 42441           |
| Independent reflections         | 3140 [R(int) = 0.0575] |
| Max. and min. transmission      | 1.0000 and 0.9535 |
| Structure solution technique    | direct methods |
| Structure solution program      | SHELXT-2014 (Sheldrick 2014) |
| Refinement method               | Full-matrix least-squares on F^2 |
| Refinement program              | SHEXL-2014 (Sheldrick 2014) |
| Function minimized              | Σw(F_o^2-F_c^2)^2 |
| Data / restraints / parameters  | 3140 / 0 / 217   |
| Goodness-of-fit on F^2          | 1.120           |
| Final R indices                 | 2551 data; I>2σ(I); R1 = 0.0413, wR2 = 0.1129 |
| all data; R1 = 0.0567, wR2 = 0.1290 |
| Weighting scheme                | w = 1/[σ^2(F_o^2)+(0.0712P)^2+0.8503P], where P = (F_o^2+2F_c^2)/3 |
| Largest diff. peak and hole     | 0.331 eÅ⁻³ and -0.623 eÅ⁻³ |
| R.M.S. deviation from mean      | 0.099 eÅ⁻³ |

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Table A.78. Atomic coordinates and equivalent isotropic atomic displacement parameters for 3-difluoro(pentafluorosulfanyl)acetylamo-1-benzofuran-2-carboxamide (Compound 11).

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<tr>
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<th>y/b</th>
<th>z/c</th>
<th>U(eq)* (Å²)</th>
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<td>0.02759(18)</td>
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<tr>
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<td>0.55317(16)</td>
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<td>0.0346(4)</td>
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<tr>
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<td>0.0379(4)</td>
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<tr>
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<td>0.19298(7)</td>
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<tr>
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<td>0.0613(6)</td>
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<tr>
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<tr>
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<tr>
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*U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.
Table A.79. Bond lengths for 3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide (Compound 11).

<table>
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<th>Bond</th>
<th>Bond length (Å)</th>
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<td>S1-F5</td>
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<td>S1-F3</td>
<td>1.5786(16)</td>
<td>S1-F4</td>
<td>1.5813(15)</td>
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<td>S1-F7</td>
<td>1.5837(14)</td>
<td>S1-C11</td>
<td>1.891(2)</td>
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<tr>
<td>F1-C11</td>
<td>1.341(2)</td>
<td>F2-C11</td>
<td>1.332(2)</td>
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<td>O2-C10</td>
<td>1.209(2)</td>
<td>O3-C9</td>
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<td>N1-C2</td>
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<tr>
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<td>1.402(3)</td>
<td>C4-C5</td>
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Table A.80. Bond angles for 3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide (Compound 11).

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<tr>
<th>Bonding Atoms</th>
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<th>Bonding Atoms</th>
<th>Bond angle (°)</th>
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<tbody>
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<td>F6-S1-F3</td>
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</tr>
<tr>
<td>F5-S1-F3</td>
<td>178.13(10)</td>
<td>F6-S1-F4</td>
<td>89.12(10)</td>
</tr>
<tr>
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<td>F3-S1-F4</td>
<td>90.29(9)</td>
</tr>
<tr>
<td>F6-S1-F7</td>
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<td>F5-S1-F7</td>
<td>89.43(9)</td>
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<tr>
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<td>F4-S1-F7</td>
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<td>89.79(9)</td>
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<tr>
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<td>105.26(14)</td>
</tr>
<tr>
<td>C10-N1-C2</td>
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</tr>
<tr>
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</tr>
<tr>
<td>O1-C1-C9</td>
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<td>C1-C2-N1</td>
<td>121.60(17)</td>
</tr>
<tr>
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<td>N1-C2-C3</td>
<td>131.26(17)</td>
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<tr>
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</tr>
<tr>
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<td>O1-C4-C5</td>
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</tr>
<tr>
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</tr>
<tr>
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<td>C5-C6-C7</td>
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<td>119.4</td>
<td>C7-C6-H6</td>
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</tr>
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<td>C7-C8-C3</td>
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<tr>
<td>C7-C8-H8</td>
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<tr>
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<td>C10-C11-S1</td>
<td>112.71(14)</td>
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Table A.81. Anisotropic atomic displacement parameters for 3-difluoro(pentafluorosulfanyl)acetylamo -1-benzofuran-2-carboxamide (Compound 11).

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<th>U_{23} (Å²)</th>
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<tr>
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<td>0.0058(6)</td>
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<tr>
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<tr>
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<td>0.0005(7)</td>
<td>0.0002(7)</td>
</tr>
<tr>
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<td>0.0129(9)</td>
<td>0.0143(9)</td>
<td>0.0025(7)</td>
<td>0.0002(7)</td>
<td>0.0007(7)</td>
</tr>
<tr>
<td>C4</td>
<td>0.0100(9)</td>
<td>0.0130(9)</td>
<td>0.0158(9)</td>
<td>0.0003(7)</td>
<td>0.0006(7)</td>
<td>0.0010(7)</td>
</tr>
<tr>
<td>C5</td>
<td>0.0149(10)</td>
<td>0.0214(10)</td>
<td>0.0163(10)</td>
<td>0.0069(8)</td>
<td>0.0018(8)</td>
<td>0.0016(8)</td>
</tr>
<tr>
<td>C6</td>
<td>0.0196(11)</td>
<td>0.0181(10)</td>
<td>0.0260(11)</td>
<td>0.0101(8)</td>
<td>0.0033(9)</td>
<td>-0.0015(8)</td>
</tr>
<tr>
<td>C7</td>
<td>0.0197(11)</td>
<td>0.0123(9)</td>
<td>0.0297(12)</td>
<td>0.0022(8)</td>
<td>0.0027(9)</td>
<td>-0.0031(8)</td>
</tr>
<tr>
<td>C8</td>
<td>0.0150(9)</td>
<td>0.0142(9)</td>
<td>0.0201(10)</td>
<td>-0.0009(8)</td>
<td>0.0011(7)</td>
<td>-0.0015(8)</td>
</tr>
<tr>
<td>C9</td>
<td>0.0116(9)</td>
<td>0.0133(9)</td>
<td>0.0170(9)</td>
<td>-0.0034(7)</td>
<td>0.0023(7)</td>
<td>-0.0004(7)</td>
</tr>
<tr>
<td>C10</td>
<td>0.0158(10)</td>
<td>0.0159(10)</td>
<td>0.0130(9)</td>
<td>-0.0006(7)</td>
<td>0.0008(7)</td>
<td>-0.0024(7)</td>
</tr>
<tr>
<td>C11</td>
<td>0.0267(11)</td>
<td>0.0167(10)</td>
<td>0.0150(10)</td>
<td>-0.0007(8)</td>
<td>0.0059(8)</td>
<td>-0.0033(8)</td>
</tr>
</tbody>
</table>

The anisotropic atomic displacement factor exponent takes the form: \(-2π²[h^2a^2U_{11}+\ldots+2ha'b'U_{12}]\).
Table A.82. Hydrogen atomic coordinates and isotropic atomic displacement parameters for
3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide
(Compound 11).

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>0.7929</td>
<td>0.7005</td>
<td>0.3869</td>
<td>0.016</td>
</tr>
<tr>
<td>H2A</td>
<td>0.9478</td>
<td>0.9529</td>
<td>0.5629</td>
<td>0.023</td>
</tr>
<tr>
<td>H2B</td>
<td>0.9014</td>
<td>0.8111</td>
<td>0.5958</td>
<td>0.023</td>
</tr>
<tr>
<td>H5</td>
<td>0.6813</td>
<td>0.3459</td>
<td>0.6302</td>
<td>0.021</td>
</tr>
<tr>
<td>H6</td>
<td>0.5944</td>
<td>0.1201</td>
<td>0.5872</td>
<td>0.025</td>
</tr>
<tr>
<td>H7</td>
<td>0.5837</td>
<td>0.0848</td>
<td>0.4792</td>
<td>0.025</td>
</tr>
<tr>
<td>H8</td>
<td>0.6600</td>
<td>0.2708</td>
<td>0.4102</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table A.83. Hydrogen bond distances and angles for
3-difluoro(pentafluorosulfanyl)acetylamino-1-benzofuran-2-carboxamide
(Compound 11).

<table>
<thead>
<tr>
<th></th>
<th>Donor-H (Å)</th>
<th>Acceptor-H (Å)</th>
<th>Donor-Acceptor (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1-O3 (intra)</td>
<td>0.88</td>
<td>2.17</td>
<td>2.737(2)</td>
<td>122.0</td>
</tr>
<tr>
<td>N2-H2A-O3</td>
<td>0.88</td>
<td>2.10</td>
<td>2.933(2)</td>
<td>157.7</td>
</tr>
<tr>
<td>N2-H2B-F4</td>
<td>0.88</td>
<td>2.46</td>
<td>3.269(2)</td>
<td>152.9</td>
</tr>
</tbody>
</table>
Figure A.68. $^{19}$F NMR spectrum of $N$-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide (Compound 12).
Figure A.69. IR spectrum of $N$-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide (Compound 12).
Figure A.70. ORTEP (a), H⋯F contact (b), F⋯F contact of equatorial F atoms of SF$_5$ group (c), and F⋯F contact of an equatorial F atom of the SF$_5$ group and an F atom of the CF$_2$ group of

$N$-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide

(Compound 12) crystal structure.
Table A.84. Sample and crystal data for

N-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide

(Compound 12).

<table>
<thead>
<tr>
<th>Identification code</th>
<th>2-(difluoro-(pentafluorosulfanyl)-methyl)-6-methyl-4-quinazolinone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C₁₁H₅F₇N₂O₂S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>362.23 g/mol</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.019x0.097x0.512 mm</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P₁</td>
</tr>
</tbody>
</table>
| Unit cell dimensions| a = 5.0207(8) Å, α = 80.087(5)°  
                               b = 6.0282(10) Å, β = 80.007(5)°  
                               c = 11.498(2) Å, γ = 72.956(5)° |
| Volume              | 324.93(9) Å³                                                 |
| Z                   | 1                                                            |
| Density (calculated) | 1.851 g/cm³                                               |
| Absorption coefficient | 0.347 mm⁻¹             |
| F(000)              | 180                                                          |

Table A.85. Data collection and structure refinement for

N-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide (Compound 12).

<table>
<thead>
<tr>
<th>Theta range for data collection</th>
<th>3.56° to 26.00°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Index ranges</td>
<td>-6≤h≤6, -7≤k≤7, -14≤l≤14</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>6204</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>2470 [Rint = 0.0254]</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>1.0000 and 0.9202</td>
</tr>
<tr>
<td>Structure solution technique</td>
<td>direct methods</td>
</tr>
<tr>
<td>Structure solution program</td>
<td>SHELXT-2014 (Sheldrick 2014)</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Refinement program</td>
<td>SHELXL-2014 (Sheldrick 2014)</td>
</tr>
<tr>
<td>Function minimized</td>
<td>Σw(Fo²-Fc²)²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>2470 / 4 / 211</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.066</td>
</tr>
<tr>
<td>Final R indices</td>
<td>2325 data; I&gt;2σ(I); R1= 0.0288, wR2= 0.0621</td>
</tr>
<tr>
<td></td>
<td>all data; R1= 0.0323, wR2 = 0.0637</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>w=1/σ²(Fo²)+(0.0358P)²+0.0160P</td>
</tr>
<tr>
<td></td>
<td>where P=(Fo²+2Fc²)/3</td>
</tr>
<tr>
<td>Absolute structure parameter</td>
<td>0.0(0)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.235 eÅ⁻³ and -0.298 eÅ⁻³</td>
</tr>
<tr>
<td>R.M.S. deviation from mean</td>
<td>0.053 eÅ⁻³</td>
</tr>
</tbody>
</table>
Table A.86. Atomic coordinates and equivalent isotropic atomic displacement parameters for $N$-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide (Compound 12).

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)* (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.38017(15)</td>
<td>0.31277(12)</td>
<td>0.81543(8)</td>
<td>0.01653(19)</td>
</tr>
<tr>
<td>F1</td>
<td>0.0610(4)</td>
<td>0.7468(3)</td>
<td>0.77863(18)</td>
<td>0.0216(4)</td>
</tr>
<tr>
<td>F3</td>
<td>0.2996(4)</td>
<td>0.2025(3)</td>
<td>0.71595(17)</td>
<td>0.0208(5)</td>
</tr>
<tr>
<td>F2</td>
<td>0.5073(4)</td>
<td>0.7065(3)</td>
<td>0.73501(16)</td>
<td>0.0193(4)</td>
</tr>
<tr>
<td>F4</td>
<td>0.0703(4)</td>
<td>0.3518(3)</td>
<td>0.87984(17)</td>
<td>0.0249(5)</td>
</tr>
<tr>
<td>F5</td>
<td>0.4598(4)</td>
<td>0.4148(4)</td>
<td>0.91820(18)</td>
<td>0.0258(5)</td>
</tr>
<tr>
<td>F6</td>
<td>0.4583(5)</td>
<td>0.0636(3)</td>
<td>0.8887(2)</td>
<td>0.0296(5)</td>
</tr>
<tr>
<td>F7</td>
<td>0.6906(4)</td>
<td>0.2644(3)</td>
<td>0.75217(19)</td>
<td>0.0239(5)</td>
</tr>
<tr>
<td>O1</td>
<td>0.4901(5)</td>
<td>0.4633(4)</td>
<td>0.2282(2)</td>
<td>0.0182(5)</td>
</tr>
<tr>
<td>O2</td>
<td>0.0450(5)</td>
<td>0.6173(4)</td>
<td>0.5684(2)</td>
<td>0.0170(5)</td>
</tr>
<tr>
<td>N1</td>
<td>0.5139(6)</td>
<td>0.5908(4)</td>
<td>0.5229(2)</td>
<td>0.0134(6)</td>
</tr>
<tr>
<td>C4</td>
<td>0.6501(7)</td>
<td>0.6196(5)</td>
<td>0.2029(3)</td>
<td>0.0162(7)</td>
</tr>
<tr>
<td>C1</td>
<td>0.4258(7)</td>
<td>0.4385(5)</td>
<td>0.3502(3)</td>
<td>0.0156(7)</td>
</tr>
<tr>
<td>C9</td>
<td>0.2695(7)</td>
<td>0.2763(6)</td>
<td>0.4018(3)</td>
<td>0.0185(7)</td>
</tr>
<tr>
<td>N2</td>
<td>0.1473(7)</td>
<td>0.1443(5)</td>
<td>0.4462(3)</td>
<td>0.0266(7)</td>
</tr>
<tr>
<td>C3</td>
<td>0.6864(6)</td>
<td>0.6931(5)</td>
<td>0.3063(3)</td>
<td>0.0141(7)</td>
</tr>
<tr>
<td>C2</td>
<td>0.5378(6)</td>
<td>0.5720(5)</td>
<td>0.4009(3)</td>
<td>0.0129(6)</td>
</tr>
<tr>
<td>C8</td>
<td>0.8427(7)</td>
<td>0.8556(5)</td>
<td>0.2979(3)</td>
<td>0.0151(7)</td>
</tr>
<tr>
<td>C10</td>
<td>0.2717(7)</td>
<td>0.6095(5)</td>
<td>0.5954(3)</td>
<td>0.0137(7)</td>
</tr>
<tr>
<td>C5</td>
<td>0.7614(7)</td>
<td>0.6992(6)</td>
<td>0.0897(3)</td>
<td>0.0222(8)</td>
</tr>
<tr>
<td>C11</td>
<td>0.2988(7)</td>
<td>0.6155(5)</td>
<td>0.7266(3)</td>
<td>0.0146(7)</td>
</tr>
<tr>
<td>C7</td>
<td>0.9546(8)</td>
<td>0.9349(6)</td>
<td>0.1856(3)</td>
<td>0.0213(8)</td>
</tr>
<tr>
<td>C6</td>
<td>0.9138(8)</td>
<td>0.8572(6)</td>
<td>0.0836(3)</td>
<td>0.0229(8)</td>
</tr>
</tbody>
</table>

*U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.
Table A.87. Bond lengths for

\(N\)-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide

(Compound 12).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond lengths (Å)</th>
<th>Bond</th>
<th>Bond lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1-F6</td>
<td>1.566(2)</td>
<td>S1-F7</td>
<td>1.567(2)</td>
</tr>
<tr>
<td>S1-F4</td>
<td>1.571(2)</td>
<td>S1-F5</td>
<td>1.579(2)</td>
</tr>
<tr>
<td>S1-F3</td>
<td>1.5792(19)</td>
<td>S1-C11</td>
<td>1.899(3)</td>
</tr>
<tr>
<td>F1-C11</td>
<td>1.331(4)</td>
<td>F2-C11</td>
<td>1.340(4)</td>
</tr>
<tr>
<td>O1-C4</td>
<td>1.373(4)</td>
<td>O1-C1</td>
<td>1.376(4)</td>
</tr>
<tr>
<td>O2-C10</td>
<td>1.217(4)</td>
<td>N1-C10</td>
<td>1.336(4)</td>
</tr>
<tr>
<td>N1-C2</td>
<td>1.408(4)</td>
<td>N1-H1</td>
<td>0.90(2)</td>
</tr>
<tr>
<td>C4-C5</td>
<td>1.388(5)</td>
<td>C4-C3</td>
<td>1.395(4)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.359(4)</td>
<td>C1-C9</td>
<td>1.419(5)</td>
</tr>
<tr>
<td>C9-N2</td>
<td>1.143(5)</td>
<td>C3-C8</td>
<td>1.406(5)</td>
</tr>
<tr>
<td>C3-C2</td>
<td>1.427(5)</td>
<td>C8-C7</td>
<td>1.381(5)</td>
</tr>
<tr>
<td>C8-H8</td>
<td>0.95</td>
<td>C10-C11</td>
<td>1.545(5)</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.372(5)</td>
<td>C5-H5</td>
<td>0.95</td>
</tr>
<tr>
<td>C7-C6</td>
<td>1.402(5)</td>
<td>C7-H7</td>
<td>0.95</td>
</tr>
<tr>
<td>C6-H6</td>
<td>0.95</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table A.88. Bond angles for
**N-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide**

(Compound 12).

<table>
<thead>
<tr>
<th>Bonding Atoms</th>
<th>Bond Angles (°)</th>
<th>Bonding Atoms</th>
<th>Bond Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F6-S1-F7</td>
<td>89.04(12)</td>
<td>F6-S1-F4</td>
<td>89.12(12)</td>
</tr>
<tr>
<td>F7-S1-F4</td>
<td>178.00(12)</td>
<td>F6-S1-F5</td>
<td>88.95(11)</td>
</tr>
<tr>
<td>F7-S1-F5</td>
<td>90.84(11)</td>
<td>F4-S1-F5</td>
<td>89.91(11)</td>
</tr>
<tr>
<td>F6-S1-F3</td>
<td>89.05(11)</td>
<td>F7-S1-F3</td>
<td>89.81(11)</td>
</tr>
<tr>
<td>F4-S1-F3</td>
<td>89.38(11)</td>
<td>F5-S1-F3</td>
<td>177.90(11)</td>
</tr>
<tr>
<td>F6-S1-C11</td>
<td>177.93(15)</td>
<td>F7-S1-C11</td>
<td>89.20(12)</td>
</tr>
<tr>
<td>F4-S1-C11</td>
<td>92.65(13)</td>
<td>F5-S1-C11</td>
<td>89.98(13)</td>
</tr>
<tr>
<td>F3-S1-C11</td>
<td>92.03(12)</td>
<td>C4-O1-C1</td>
<td>104.9(2)</td>
</tr>
<tr>
<td>C10-N1-C2</td>
<td>122.6(3)</td>
<td>C10-N1-H1</td>
<td>118.2</td>
</tr>
<tr>
<td>C2-N1-H1</td>
<td>119.2</td>
<td>O1-C4-C5</td>
<td>125.3(3)</td>
</tr>
<tr>
<td>O1-C4-C3</td>
<td>111.5(3)</td>
<td>C5-C4-C3</td>
<td>123.2(3)</td>
</tr>
<tr>
<td>C2-C1-O1</td>
<td>112.0(3)</td>
<td>C2-C1-C9</td>
<td>131.1(3)</td>
</tr>
<tr>
<td>O1-C1-C9</td>
<td>116.9(3)</td>
<td>N2-C9-C1</td>
<td>178.0(4)</td>
</tr>
<tr>
<td>C4-C3-C8</td>
<td>119.6(3)</td>
<td>C4-C3-C2</td>
<td>104.9(3)</td>
</tr>
<tr>
<td>C8-C3-C2</td>
<td>135.5(3)</td>
<td>C1-C2-N1</td>
<td>127.4(3)</td>
</tr>
<tr>
<td>C1-C2-C3</td>
<td>106.8(3)</td>
<td>N1-C2-C3</td>
<td>125.8(3)</td>
</tr>
<tr>
<td>C7-C8-C3</td>
<td>117.4(3)</td>
<td>C7-C8-H8</td>
<td>121.3</td>
</tr>
<tr>
<td>C3-C8-H8</td>
<td>121.3</td>
<td>O2-C10-N1</td>
<td>126.9(3)</td>
</tr>
<tr>
<td>O2-C10-C11</td>
<td>119.6(3)</td>
<td>N1-C10-C11</td>
<td>113.5(3)</td>
</tr>
<tr>
<td>C6-C5-C4</td>
<td>116.2(3)</td>
<td>C6-C5-H5</td>
<td>121.9</td>
</tr>
<tr>
<td>C4-C5-H5</td>
<td>121.9</td>
<td>F1-C11-F2</td>
<td>107.9(2)</td>
</tr>
<tr>
<td>F1-C11-C10</td>
<td>109.9(3)</td>
<td>F2-C11-C10</td>
<td>111.6(3)</td>
</tr>
<tr>
<td>F1-C11-S1</td>
<td>108.6(2)</td>
<td>F2-C11-S1</td>
<td>106.2(2)</td>
</tr>
<tr>
<td>C10-C11-S1</td>
<td>112.6(2)</td>
<td>C8-C7-C6</td>
<td>121.4(3)</td>
</tr>
<tr>
<td>C8-C7-H7</td>
<td>119.3</td>
<td>C6-C7-H7</td>
<td>119.3</td>
</tr>
<tr>
<td>C5-C6-C7</td>
<td>122.1(4)</td>
<td>C5-C6-H6</td>
<td>119.0</td>
</tr>
<tr>
<td>C7-C6-H6</td>
<td>119.0</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Table A.89. Anisotropic atomic displacement parameters (Å²) for
\(N\)-\(2\)-(cyano-1-benzofuran-3-yl)-\(2,2\)-difluoro-\(2\)-pentafluorosulfanyl acetamide

(Compound 12).

\begin{table}
\begin{tabular}{|c|ccccccc|}
\hline
 & \(U_{11}\) (\(\text{Å}^2\)) & \(U_{22}\) (\(\text{Å}^2\)) & \(U_{33}\) (\(\text{Å}^2\)) & \(U_{23}\) (\(\text{Å}^2\)) & \(U_{13}\) (\(\text{Å}^2\)) & \(U_{12}\) (\(\text{Å}^2\)) \\
\hline
S1 & 0.0150(4) & 0.0186(4) & 0.0170(4) & -0.0010(3) & -0.0040(3) & -0.0057(3) \\
F1 & 0.0143(10) & 0.0211(10) & 0.0245(11) & -0.0096(8) & 0.0038(8) & 0.0028(8) \\
F2 & 0.0274(12) & 0.0145(9) & 0.0231(12) & -0.0020(8) & -0.0089(9) & -0.0067(9) \\
F3 & 0.0180(10) & 0.0227(10) & 0.0223(11) & -0.0072(8) & -0.0006(8) & -0.0119(8) \\
F4 & 0.0195(11) & 0.0325(11) & 0.0226(11) & 0.0001(9) & 0.0043(9) & -0.0130(9) \\
F5 & 0.0288(12) & 0.0346(12) & 0.0188(11) & -0.0034(9) & -0.0089(9) & 0.0125(10) \\
F6 & 0.0367(14) & 0.0249(11) & 0.0278(12) & 0.0066(9) & 0.0140(10) & 0.0093(10) \\
F7 & 0.0237(10) & 0.0327(11) & 0.0322(12) & -0.0038(9) & -0.0024(9) & -0.0005(9) \\
O1 & 0.0178(13) & 0.0186(12) & 0.0194(13) & 0.0052(10) & 0.0039(10) & 0.0045(10) \\
O2 & 0.0108(12) & 0.0194(11) & 0.0221(13) & 0.0002(9) & 0.0045(10) & -0.0063(9) \\
N1 & 0.0101(14) & 0.0147(12) & 0.0146(15) & 0.0022(11) & 0.0025(12) & 0.0040(11) \\
C4 & 0.0129(17) & 0.0135(15) & 0.0192(18) & 0.0036(13) & 0.0010(14) & 0.0012(13) \\
C1 & 0.0109(16) & 0.0153(16) & 0.0181(18) & 0.0025(13) & 0.0011(13) & 0.0003(13) \\
C9 & 0.0143(17) & 0.0167(16) & 0.0259(19) & 0.0076(14) & 0.0058(15) & 0.0018(14) \\
N2 & 0.0253(18) & 0.0190(15) & 0.0390(19) & 0.0076(14) & 0.0039(15) & 0.0091(14) \\
C3 & 0.0094(16) & 0.0138(15) & 0.0171(17) & 0.0023(13) & 0.0030(13) & 0.0008(12) \\
C2 & 0.0082(15) & 0.0129(15) & 0.0152(16) & 0.0016(12) & 0.0030(13) & 0.0014(12) \\
C8 & 0.0118(17) & 0.0143(16) & 0.0175(19) & 0.0015(13) & 0.0024(13) & 0.0012(13) \\
C10 & 0.0120(16) & 0.0085(15) & 0.0205(17) & 0.0027(13) & 0.0033(14) & 0.0018(12) \\
C5 & 0.0208(19) & 0.0257(18) & 0.0181(18) & 0.0036(15) & 0.0042(15) & 0.0017(15) \\
C11 & 0.0096(16) & 0.0126(15) & 0.0203(19) & 0.0042(13) & 0.0005(14) & 0.0013(13) \\
C7 & 0.0159(17) & 0.0182(16) & 0.0272(15) & 0.0028(15) & 0.0003(15) & 0.0052(13) \\
C6 & 0.0228(19) & 0.0221(17) & 0.0181(17) & 0.0017(14) & 0.0011(15) & 0.0019(15) \\
\hline
\end{tabular}
\end{table}

Table A.90. Hydrogen atomic coordinates and isotropic atomic displacement parameters for

\(N\)-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide
(Compound 12).

<table>
<thead>
<tr>
<th></th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq) (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>0.661(6)</td>
<td>0.609(6)</td>
<td>0.552(3)</td>
<td>0.02</td>
</tr>
<tr>
<td>H8</td>
<td>0.8701</td>
<td>0.9087</td>
<td>0.3669</td>
<td>0.018</td>
</tr>
<tr>
<td>H5</td>
<td>0.7337</td>
<td>0.6472</td>
<td>0.0204</td>
<td>0.027</td>
</tr>
<tr>
<td>H7</td>
<td>1.0616</td>
<td>1.0445</td>
<td>0.1773</td>
<td>0.026</td>
</tr>
<tr>
<td>H6</td>
<td>0.9941</td>
<td>0.9159</td>
<td>0.0078</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Table A.91. Hydrogen bond distances and angles for N-(2-cyano-1-benzofuran-3-yl)-2,2-difluoro-2-pentafluorosulfanyl acetamide (Compound 12).

<table>
<thead>
<tr>
<th>Donor-H (Å)</th>
<th>Acceptor-H (Å)</th>
<th>Donor-Acceptor (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1-O2</td>
<td>0.90(2)</td>
<td>1.99(3)</td>
<td>2.859(3)</td>
</tr>
<tr>
<td>C5-H5-F4</td>
<td>0.95</td>
<td>2.63</td>
<td>3.340(4)</td>
</tr>
</tbody>
</table>

Figure A.71. Mass Spectrum of SF₅CF₂H
List of Abbreviations

THF: Tetrahydrofuran
DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene

NMR: Nuclear magnetic resonance

FT-IR: Fourier transform infrared spectroscopy

ACE: Angiotensin converting enzyme

TFA: Trifluoroacetic acid

ATR-IR: Attenuated total reflectance infrared spectroscopy

HRMS: High resolution mass spectroscopy

RNA: Ribonucleic acid

BRCA2: Breast cancer type 2 susceptibility gene

COX-2: Cyclooxygenase 2

PGH₂: Prostaglandin endoperoxide synthase 2

LCD: Liquid Crystal Display

ECF: Electrochemical Fluorination

TEMPO: 2,2,6,6-Tetramethyl-1-piperidinyloxy, free radical