DISS. ETH NO. 27162

Fluorination of Heteroatoms – Chalcogens and Beyond

A thesis submitted to attain the degree of

DOCTOR OF SCIENCES of ETH ZURICH

(Dr. sc. ETH Zurich)

presented by

Dustin Bornemann

MSc, University of Zurich

born on 22.11.1991

citizen of Germany

accepted on the recommendation of

Prof. Dr. Antonio Togni

Prof. Dr. Hansjörg Grützmacher

2020

Dubium sapientiae initium.

- René Descartes

Acknowledgements

A successful doctorate is by no means the achievement of an individual, but rather the result of several years of co-operation between a broad spectrum of people. I had the great pleasure and privilege to get to know many scientist, young and older, work with and learn from them during my time here at the ETH Zürich. Thus, I want to dedicate this section to the many people, mentors and colleagues, friends and family, without whom I would not have been able to complete this thesis.

Firstly, I would like to sincerely thank **Prof. Dr. Antonio Togni** for giving me the opportunity to conduct my Ph.D. studies in his group.

Antonio, maybe unbeknownst to you, our first encounter goes back almost ten years to 2011 when you first taught AC(AC)-I. Your iconic opening of a can of RedBull®, whilst introducing the *molecule of the week* taurine in your typical laid-back and at the same time enthusiastic manner of teaching, stuck to me throughout my entire studies. It was a pleasure to go to your lectures in 2011 and it became a wonderful learning experience years later when I had the chance to help you prepare this course that first pushed me towards inorganic chemistry.

I am grateful, that I was given the opportunity to work with, and learn from you, for the continuous support and the almost infinite freedom I enjoyed when it came to choosing research topics to pursue within my doctoral studies.

Furthermore, I would like to thank **Prof. Dr. Hansjörg Grützmacher** for taking over the role of my co-examiner, the helpful discussions about main group chemistry, the valuable input, and his enthusiasm for my studies in phosphorus chemistry.

The past years have had a lasting impact on me. Even if the doctorate was stressful, ungrateful, frustrating, and unbelievably challenging at times, the positive experiences have far outweighed the negative ones. This is not least thanks to former and current group members. I am sure that your support in the scientific as well as the interpersonal domain was vital to the success of my doctoral studies. I would therefore like to express my sincerest gratitude to all of you. First of all, my partner in crime **Fabian Brüning**, I am unbelievably glad that I found an arguably better dressed but equally wacky counterpart and friend in you when I started my doctorate in the group. I would like to thank you for the immensely fun times in and outside the lab. Thank you for the many great evenings, for the shared times as "Oberassistenten" of ATs AC(AC)-I course and the rich, always entertaining coffee breaks at Hönggerberg. Without you, the last years would certainly have been much less bearable.

My current and former lab mates in H238, **Roxan Calvo**, **Jorna Kalim**, **Ewa Pietrasiak** and **Sebastian "the Don" Küng** also deserve praise. I am obliged to thank all of you for

your unlimited tolerance of the chaos that I call my hood(s), desk and mind. More specifically, I want to thank Sebastian for bearing with me as your teacher, Ewa for answering my frequently uninformed questions about tellurium-related problems, Jorna and Roxan for letting me abuse your hoods (and sometimes desks) when I ran out of space. I find it extraordinary how little complaints I've heard throughout the years and I want you to know how much I appreciated that. Thank you guys, I've always felt welcome the lab and whenever I was looking for advice my questions were met with an open ear. Working with every one of you has been good fun!

Cody "Schmody" Ross Pitts within the past years you have become both a mentor and a good friend. I enjoyed the time we spent together, working on projects with you and the frequent schmoffee breaks. I am glad that whilst I learnt a lot about the American culture (Reeses, Thanksgiving, hourlong phoning sessions and more) from you, you were able to pick up some German phrases that will come in handy one day, trust me. All the best in your pursuit of your independent career, you'll make it!

Moreover, I am indebted to all of my students, working with you and witnessing the eagerness with which you wanted to learn about chemistry and the speed with which you picked up on new techniques is among the most rewarding experiences that I made within my doctoral studies. **Lukas Schlemper**, thank you for choosing me as the supervisor not only for a semester project but also for a subsequent master thesis. You are certainly one of the most practically gifted students I have encountered throughout my years as a chemist. All the best in Morandi's group! As a farewell gift, you'll inherit my collection of precious IK-Schlenks! Thank you to **Carmen Ziegler** for the incredible diligence and motivation with which you carried out your semester project. You'll do great in industry! **Lionel Wettstein**, we still have a part of your master thesis ahead and I am very much looking forward to it. You are an extremely smart guy and not least because we share a similar chemical pedigree I have high hopes for your future as a Ph.D. student in chemistry.

Gratitude is owed to **Prof. Dr. Antonio Mezzetti** for his open ears whenever I had an organometallics or catalysis related question. I also want to thank all other past and present members of the Togni group, **Mona Wagner**, **Carl-Philipp Rosenau**, **Alex Lauber**, **Harutake Kajita**, **Pascal Tripet**, **Benson Jelier**, **Dmitry Katajev**, **Kun Zhang**, **Pascal Engl**, **Niccolò Bartalucci**, **David Rombach**, **Phil Liebing**, and the Mezzetti group members **Alessandro Passera**, **Raffael Huber**, **Lorena De Luca**, **Harikrishnan Jayaprakash** and **Melanie Strauss** for the for the relaxing atmosphere and great working environment.

A special thanks is owed to my family, especially **Kerstin Bornemann, David Bornemann** and **Matthias Schulz** for all the love, care, fun, support and excitement that I was able to experience thanks to you. I am grateful to my friends in- and outside of the university especially **Reto Bollmann, Manuel Hernandez, Hans Zeller** and **Bastian Buman** for the fun and excitement (and occasionally too much booze) we shared and for another Wacken or Greenfield festival to come. Thanks to my B-33 flat mates **Vicktoria Häffner, Tobias Bärtsch, Max Paulus, Raphaela Kreiser** for the entertaining evenings, jogging sessions, BBQs and generally everything that happened the past three and a half years in our beautiful house.

Jana, ich möchte dich an dieser Stelle gesondert erwähnen. Du bist sicherlich die Person, der der grösste Dank gebührt. Die letzten Jahre hast du mich stets unterstützt, hinterfragt, herausgefordert, eines Besseren belehrt und mir die Stirn geboten, wenn es sein musste. Ich bin in den drei Jahren des Doktorats vor Allem durch dich persönlich gereift und dir dafür von Herzen dankbar. Ich freue mich auch in Zukunft viele neue Erfahrungen mit dir zu sammeln, zu reisen, zu lernen, zu diskutieren und zu wachsen. Danke für die wundervolle Zeit. MM&BBB

Contents

List of Publications

1. **Bornemann, D.**; Pitts, C. R.; Wettstein, L.; Brüning, F.; Küng, S.; Guan, L.; Trapp, N.; Grützmacher, H.; Togni, A. "Deoxygenative Fluorination of Phosphine Oxides: A General Route to Fluorinated Organophosphorus(V) Compounds and Beyond", *Angew. Chem. Int. Ed*, **2020**, *59*, 2-8. DOI: 10.1002/anie.202010943

2. **Bornemann, D.**; Schlemper, L.; Trapp, N.; Togni, A. "Expanding the Scope of Water-Stable Rhenium(V)-NHC Complexes – Synthesis, Characterization, and Derivatization" *Eur. J. Inorg. Chem.* **2020**, 1004-1010. DOI: 10.1002/ejic.201901077

3. Brüning, F.; Pitts, C. R.; Kalim, J.; **Bornemann, D.**; Ghiazza, C.; de Montmillon, J.; Trapp, N.; Billard, T.; Togni, A. "Difluoro(aryl)(perfluoroalkyl)-λ⁴-sulfanes and Selanes: Missing Links of Trichloroisocyanuric Acid/Potassium Fluoride Chemistry" *Angew. Chem. Int. Ed.* **2019**, *58*, 18937-18941. DOI: 10.1002/ange.201910594

4. **Bornemann, D.**; Pitts, C. R.; Ziegler, C. J.; Pietrasiak, E.; Trapp, N.; Santschi, N.; Togni, A. "Pentafluoro(aryl)-λ⁶-tellanes and Tetrafluoro(aryl)(trifluoromethyl)-λ⁶-tellanes: From SF5 to the TeF5 and TeF4CF3 Groups" *Angew. Chem. Int. Ed.* **2019**, *58*, 12604-12608. **[Hot Paper]** DOI: 10.1002/anie.201907359

5. Häfliger, J.; Pitts, C. R.; **Bornemann, D.**; Käser, R.; Santschi, N.; Charpentier, J.; Otth, E.; Trapp, N.; Verel, R.; Lüthi, H. P.; Togni, A. "Substituent-controlled, Mild Oxidative Fluorination of Iodoarenes: Synthesis and Structural Study of Aryl I(III)- and I(V)-Fluorides" *Chem. Sci.* **2019**, *10*, 7251-7259. DOI: 10.1039/c9sc02162k

6. Pitts, C. R.; **Bornemann, D.**; Liebing, P.; Santschi, N.; Togni, A. "Making the SF_5 Group More Accessible: A Gas Reagent-free Approach to Aryl Tetrafluoro-λ⁶-sulfanyl Chlorides" *Angew. Chem. Int. Ed.* **2019**, *58*, 1950-1954. DOI: 10.1002/anie.201812356

7. Liebing, P.; Pietrasiak, E.; Otth, E.; Kalim, J.; **Bornemann, D.**; Togni, A. "Supramolecular Aggregation of Perfluoroorganyl Iodane Reagents in the Solid State and in Solution" *Eur. J. Org. Chem.* **2018**, *27-28*, 3771-3781. DOI: 10.1002/ejoc.201800358

Conference Presentations

International Conference on Heteroatom Chemistry (ICHAC), Prague, Czech Republic, Summer **2019** Oral Presentation: "Synthesis, Structure and Reactivity of Pentafluoro(aryl)-λ^6-tellanes"

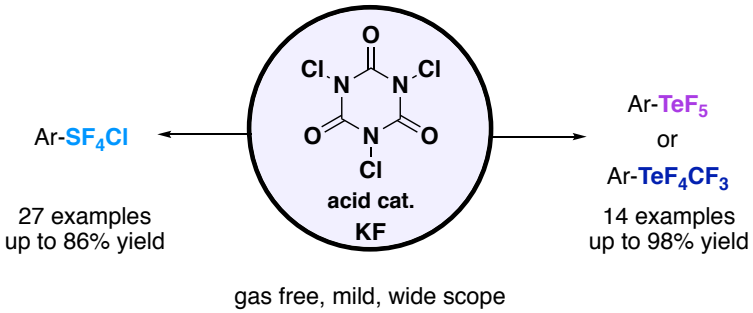
ETH Symposium on the Occasion of Departmental Evaluation by an International Panel, Zurich, Switzerland, Spring **2019**, Poster Presentation: "A General Approach to Oxidative Polyfluorination of Heteroatoms: Chalcogens and Beyond"

ETH LAC Christmas Symposium, Zurich, Switzerland, Winter **2018** Oral Presentation: "A General Approach to Oxidative Polyfluorination of Heteroatoms: Making the SF_5 Group and its Kin More Accessible"

Abstract

In the frame of this doctoral thesis, straightforward, gas-free fluorination procedures for different main group elements mostly bound to an aromatic organic framework were developed and investigated in detail. Thus, the current general problem of a still lacking general and mild methodology for the oxidative fluorination of heteroatoms was tackled and partly solved.

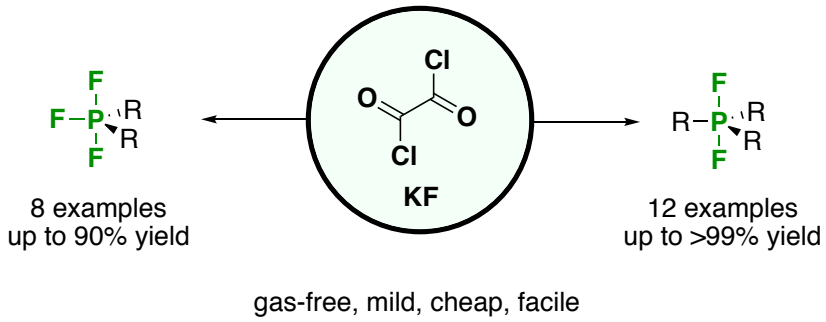
The first part of this work is concerned with the fluorination of diaryl disulfides to form aryl-SF_4Cl species, key-intermediates in the synthesis of sought-after SF_5-bearing molecules. Literature known methods for the preparation of such compounds exclusively rely on the use of highly toxic, hazardous, gaseous oxidants such as fluorine or chlorine gas, which made work in this field difficult and unattractive, especially for academic research labs. In this thesis, the dependence on gaseous reagents en-route to such compounds was completely overcome by using trichloroisocyanuric acid (TCICA), a solid, easy-to-use, stable oxidizing agent, in combination with potassium fluoride (KF) and catalytic amounts of acid (trifluoroacetic acid, TFA). The newly found approach allowed access to a number of already known as well as hitherto undescribed aryl-SF_4Cl, -SF_4R compounds. Finally, the conversion of the former into their SF_5 derivatives was also demonstrated. X-ray diffraction analyses enabled us to present and discuss the first aryl-SF_4Cl crystal structure.



In the second part of this thesis the experience gained with disulfides was used to investigate the oxidative fluorination of diaryl ditellurides. After optimization of the method for the new substrate class it was possible to synthesize a number of aryl-TeF_5 compounds by conversion of the corresponding ditellurides with TCICA/KF in one step. The products were investigated in detail by NMR spectroscopy (^{1}H, ^{13}C, ^{19}F, ^{125}Te) and X-ray diffraction analysis. The latter allowed to gain insights into the solid-state structure of aryl-TeF_5 compounds and to compare them with corresponding SF_5 derivatives with respect to their structure and bonding properties. Finally, the compounds were examined for their stability and reactivity with olefins and nucleophiles. It became clear that, while it is arguably much more reactive than SF_5, the TeF_5 group is much more stable than previously assumed and,

in contrast to earlier publications, aryl-TeF_5 species are not suitable as difluorinating agents of unsaturated hydrocarbons.

The third part of the work concentrated on the preparation of fluorinated phosphorus compounds, mainly in the form of difluoro- (R_3PF_2) and trifluoroorganophosphoranes (R_2PF_3) and their salts. Known methods to access such species suffered from similar problems as those used for the preparation of TeF_5- and SF_5-bearing molecules. Hence, the TCICA/KF process was applied to triarylphosphines, unfortunately not yielding satisfying results. Consequently, an improved method for the preparation of such compounds was developed.

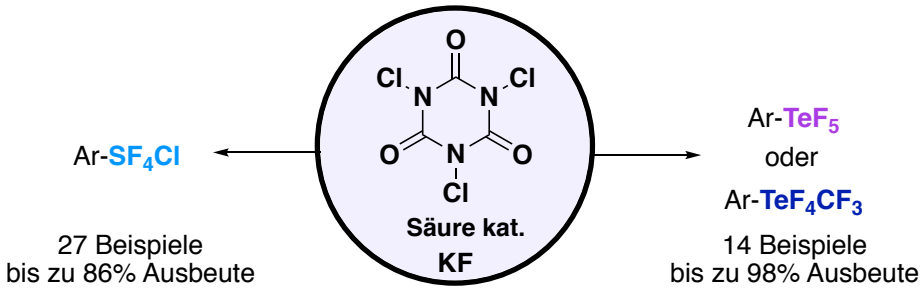


This method uses organic phosphine oxides as starting materials and converts them with oxalyl chloride ($(COCl)_2$) and KF in a one-step synthesis to the corresponding fluorinated derivatives. It was thus possible not only to produce known fluorophosphoranes in a simpler and more convenient way, but also to provide access to numerous previously unknown R_3PF_2 and R_2PF_3 derivatives. The compounds have been spectroscopically investigated and characterized, and a number of new crystal structures of these compounds have been obtained. Furthermore, using the obtained R_2PF_3 species, two examples of $[R_2PF_2]^+$ species were accessed by fluoride abstraction. Finally, the method was extended to allow the synthesis of Ph_3AsF_2 and Ph_3SbF_2 in good yields.

Zusammenfassung

Im Rahmen dieser Doktorarbeit wurden einfache, gasfreie Fluorierungsverfahren für verschiedene Hauptgruppenelemente, die in einem aromatischen organischen Gerüst gebunden sind, entwickelt und eingehend untersucht. So wurde das häufige Problem einer allgemeinen Methodik für die (oxidative) Fluorierung von Heteroatomen in Angriff genommen und in mancher Hinsicht gelöst.

Der erste Teil dieser Arbeit behandelt die Fluorierung von Diaryldisulfiden unter der Bildung von SF_4Cl-substituierten Molekülen, wichtige Vorstufen zur Synthese von hochbegehrten SF_5-tragenden Molekülen. Die bisherigen, literaturbekannten Methoden zur Herstellung dieser Verbindungen beruhten stets auf der Verwendung von hochgiftigen, gefährlichen, gasförmigen Fluorierungsmitteln wie Fluor- oder Chlorgas, was die Arbeit auf dem Gebiet für universitäre Syntheselabors schwierig und unattraktiv machte. Im Zuge dieser Doktorarbeit gelang es die Abhängigkeit von gasförmigen Reagenzien zur Herstellung solcher Verbindungen vollständig zu überwinden indem Trichlorisocyanursäure (TCICA), ein festes, einfach zu handhabendes, stabiles Oxidationsmittel, anstatt der gasförmigen Reagenzien in Kombination mit Kaliumfluorid (KF) und katalytischen Mengen an Säure (Trifluoressigsäure, TFA) eingesetzt wurde. Dadurch wurde es möglich eine Reihe an bereits bekannten aryl-SF_4Cl Verbindungen herzustellen und in ihre SF_5-Derivate zu überführen. Weiterhin wurden bisher nicht beschriebene aryl-SF_4Cl und -SF_4R Verbindungen mittels des TCICA/KF Verfahrens hergestellt und vollständig charakterisiert. Schliesslich wurden erstere ebenfalls in ihre SF_5-Analoga überführt. Einige neue aryl-SF_5 Verbindungen und zum ersten Mal ein aryl-SF_4Cl Derivat konnten röntgenkristallographisch charakterisiert werden.

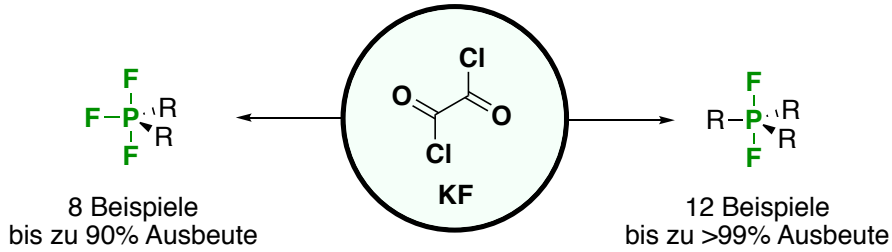


gasfrei, mild, grossser Reaktionsumfang

Im zweiten Teil dieser Arbeit wurde die mittels Disulfiden erworbene Erfahrung der Einsetzbarkeit des TCICA/KF Verfahrens genutzt, um die oxidative Fluorierung von Diarylditelluriden zu untersuchen. Nach Optimierung der Methode für die neue Substratklasse war es möglich, eine Reihe an aryl-TeF_5 Verbindungen durch Umsatz der

Ditelluride mit TCICA/KF in einem Schritt darzustellen. Die Verbindungen wurden mittels NMR (^{1}H, ^{13}C, ^{19}F, ^{125}Te) sowie Röntgenkristallanalyse eingehend untersucht, was einen ersten Einblick in die Festkörperstruktur von aryl-TeF_5 Verbindungen gewährte. Letzteres ermöglichte einen aufschlussreichen Vergleich und eine detaillierte Analyse der Struktur und Bindungsverhältnisse der TeF_5 und SF_5 Gruppen. Abschliessend wurden die Verbindungen auf ihre Stabilität und Reaktivität mit Olefinen sowie Nukleophilen untersucht. Es wurde dabei klar, dass die TeF_5 Gruppe wesentlich stabiler ist als bisher angenommen und, anders als beschrieben, aryl-TeF_5 Spezies als Difluorierungsmittel von ungesättigten Kohlenwasserstoffen ungeeignet sind.

Der dritte Teil der Arbeit konzentrierte sich auf die Herstellung von fluorierten Phosphorverbindungen hauptsächlich in Form von Difluor- (R_3PF_2) sowie Trifluororganophosphoranen (R_2PF_3) und deren Salzen. Die bisherigen Methoden litten unter ähnlichen Problemen wie die zur Herstellung von TeF_5 und SF_5 Spezies und so wurde das TCICA/KF Verfahren hier ebenfalls getestet, lieferte jedoch ungenügende Resultate. Folglich wurde eine verbesserte Methode zur Darstellung solcher Verbindungen entwickelt.



gasfrei, mild, günstig, einfach

Diese verwendet organische Phosphanoxide als Startmaterialien und setzt sie mit Oxalylchlorid ($(COCl)_2$) und KF in einer Ein-Schritt-Synthese zu den entsprechenden fluorierten Derivaten um. Es war somit möglich nicht nur bekannte Fluorphosphorane auf einfacherem und günstigerem Wege herzustellen, sondern auch den Zugang zu zahlreichen bisher unbekannten R_3PF_2 und R_2PF_3 Verbindungen zu ermöglichen. Die Verbindungen wurden spektroskopisch untersucht und charakterisiert, dabei wurde nicht zuletzt auch eine Reihe dieser Verbindungen kristallographisch charakterisiert. Weiterhin ermöglichte die Verwendung der erhaltenen R_2PF_3 Spezies, die Synthese zweier Phosphoniumsalze vom Typ $[R_2PF_2]^+$ durch Fluoridabstraktion. Schlussendlich erlaubte die Methode auch die Synthese von Ph_3AsF_2 und Ph_3SbF_2.

Introductory Remarks

In the following, the structure of this work is briefly elaborated to provide the reader with a general overview of its content. This thesis is composed of six chapters. The first three chapters each focus on the fluorination of a different element. Therefore, each chapter comprises an introduction into the element, its historical significance, modern applications and fluorine chemistry. These introductory sections are followed by descriptions and discussions of the experimental results obtained throughout this work and end with a summary of each chapter.

Chapter 1 provides a short overview of the element fluorine, its discovery, older and modern applications as well as its significance in the chemistry of the 21st century.

Chapter 2 discusses a novel, gas reagent-free route for the synthesis of R-SF_4Cl and R-SF_5 compounds, derivatization reactions of the former and physicochemical properties of both in the form of NMR spectroscopy as well as solid-state analyses.

Chapter 3 describes the synthesis of R-TeF_5 molecules, provides a first in-depth solid-state study of those exotic compounds, explores their (un)reactivity and gives a detailed comparison of the TeF_5 and SF_5 groups.

Chapter 4 elaborates on the desoxyfluorination of various group 15 elements, strongly focusing on phosphine oxides as the substrates. The chapter describes a new facile way for the synthesis of polyfluorinated phosphoranes and their NMR spectroscopic and solid-state properties.

Chapter 5 concludes the thesis and gives an outlook for future fluorine chemists and chapter 6 gives details about the experiments conducted throughout this work.

Due to the heterogeneity of this thesis, dealing with a variety of elements, compounds and compound classes, no consecutive numbering of the various species was applied and instead, the compounds are divided into subseries which are named accordingly. The following short list shall provide an overview of the compound subseries under study.

Chapter 2 mentions disulfides comprised within subseries **S-1**, R-SF_4Cl species which belong to series **S-2**, R-SF_3 and RSF_5 species in series **S-3** and **S-4**, respectively and finally R_2SF_4 compounds within subseries **S-5**.

Analogously chapter 3 comprises ditellurides as series **Te-1**, R-TeF_5 species in the form of series **Te-2** as well as R-$TeCF_3$ and R-TeF_4CF_3 in series **Te-3**.

Finally, chapter 4 mentions various phosphine oxides as the **P-1** series, difluorophosphoranes and trifluorophosphoranes as the **P-2** and **P-3** series, respectively and tetrafluorophosphates as series **P-4**. Pentafluorophosphates are comprised in series **P-5** and their tetrafluorophosphoranes analogues in series **P-6**. Series **P-7** comprises the two difluorophosphonium species obtained throughout this thesis.

Chapter 1

The Element Fluorine: A Brief Introduction

1.1 Remarks

All topics concerning the main part of this dissertation are closely related to the element fluorine, its applications and main group chemistry. The following introduction to the element is intended to arouse the interest of the reader and help to highlight the historical and scientific significance of fluorine and fluorine-containing compounds. For further reading, the insightful book by Alain Tressaud titled *Fluorine: A Paradoxical Element* is recommended.[1]

1.2 Fluorine – History, Applications and Shortcomings

The element fluorine occupies an extraordinary position in the periodic table. The halogen is not only the most electronegative (by definitions of Pauling: $\chi = 3.98$ or $\chi = 4.42$), element but also forms the strongest single bonds to "the element of life" carbon.[2] Its extraordinarily high electronegativity results in a correspondingly high reactivity, rendering the element the most reactive of the periodic table. This property was impressively demonstrated by Neil Bartlett in 1962 who used the highly fluorinated PtF_6 in a reaction with Xe resulting in the first observed oxidation of the, thought to be chemically inert, noble gas to $XeFPtF_5$ (and $XeFPt_2F_{11}$).[3] Interest in the element and its compounds, however, was present much before the 20th century. The oldest known applications for fluorine date back to the Late Bronze Age.[1,4] Inhabitants of the Aegean islands discovered the ornamental properties of fluorides, especially fluorite, resulting in the production of decorative items and jewelry. Its relatively high abundance in the Earth's crust (0.059%) made compounds of the element fairly accessible even in ancient times.[5] The use of fluorides, however, extended beyond the superficial reasons of pure aesthetics. "Medicinal" applications of fluorite crystals and powders as therapeutics to treat a variety of ailments, stretching from drunkenness to kidney stones, have already been known to the ancient Romans and continued until modern times.[1,6] A more fundamental understanding of potential applications for the first fluorinated species, however, was only obtained in the Renaissance. The first description of fluorspar (CaF_2) was provided by the "*father of mineralogy*" Georgius Agricola in 1529, rendering the mineral the earliest identified fluoride salt.[1,7] The German scientist also proposed the name "fluores" (lat: *fluere* "to flow") for fluorite containing rocks which were, at the time, used to assist the extraction of metals from ores, rendering the resulting melt less viscous. The expression later evolved into the modern name fluorine. A common feature of the pre-modern applications of fluorine was that they exclusively involved the use of fluorine-containing compounds, mainly fluorides, rather than elemental F_2. A fact easily understood when examining the properties of the element.

As initially mentioned, fluorine is the most reactive element. With a standard reduction potential of 2.87 V fluorine easily oxidizes the main components of the Earth's atmosphere N_2, O_2 and even noble gases except He and Ne. It thus comes as no surprise that elemental fluorine cannot be found in nature and thus access to the lightest halogen is far from straightforward. However, the only known exception is the radiolysis of uranium-contaminated fluorspar in which enclosed F_2 is formed and is responsible for the caustic smell of the pulverized mineral.[8] Due to the necessary technical means, the isolation of pure elemental fluorine only succeeded in the late nineteenth century. French chemist Henri Moissan accomplished its isolation in 1886 by electrolysis of KHF_2 in HF, resolving one of the most challenging problems of inorganic chemistry at the time (or perhaps ever) and was consequently awarded the Nobel Prize in chemistry for his discoveries in 1906 (Picture 1).[1,9] To point out the difficulty of the task, Moissan himself noted in his "*Le Fluor et ses Composés*" that it took him more three years to even be able to observe the first useful results in his attempts of the isolation of fluorine gas.

Picture 1: Moissan's apparatus for the isolation of F_2. From Henri Moissan Museum, Faculty of Pharmacy, University Paris V, Photo Alain Tressaud.

Although improvements to Moissan's method have since been made, its fundamental principles, namely the use of KHF_2 in HF, are still the state-of-the-art procedure for the industrial production of fluorine gas. Following the isolation of the halogen, its importance for industrial as well as academic research has increased dramatically.[10] With initial industrial applications of the halogen in the early 20th century concentrating on the production of halogenated hydrocarbons (chlorofluorocarbons, CFCs) as cooling gases and fire-extinguishing agents or the production of more tangible goods like Teflon or fluorine-containing toothpaste, the focus of fluorine chemistry quickly shifted towards an entirely different field in the 1950s, the life sciences.[1,11] Recent decades have witnessed a significantly increased attention paid to the halogen in both academia and industry. Noteworthy is especially the field of organofluorine chemistry. The introduction of fluorine or fluorinated substituents into organic molecules can drastically affect their physicochemical properties.

Changes in behavior that are frequently observed upon fluorination of organic molecules include increased lipophilicity, differences in solubility, molecular conformation, melting and boiling points, receptor affinities, cellular permeability as well as metabolic stabilities and more.[12–14] Some of these introduced differences are highly interesting for applications in medicinal chemistry, agrochemistry and materials, frequently leading to molecules with overall advantageous properties when compared to their non-fluorinated counterparts.[15,16] Fluorine's impact on these fields was tremendous, as can easily be shown when examining the development of the application of fluorinated molecules in the course of time. While the market knew only 2% fluorine-containing molecules used in medicinal chemistry in the 1970s, their market share rose to over 18% in the early 21st century. Similar trends can be found for agrochemistry where 3% of the active ingredients contained fluorine in the 1970s, compared to 50% today.[17] This extraordinary success of fluorine chemistry naturally led to a steeply growing interest in better, more selective, milder and cheaper methodologies that would allow for the (late-stage) introduction of fluorine and fluorinated groups into organic molecules. So, it is hardly surprising that methods for that purpose became more and more advanced and are, nowadays, fairly abundant, allowing a plethora of transformations with a remarkable diversity of products.

However, in contrast to organofluorine chemistry, analogous progress has not been made in the field of inorganic, more specifically, main group chemistry. Fluorination reactions and methodologies for main group elements are still significantly underexplored and while contributions towards the field of inorganic fluorine chemistry do increase, standardized, facile approaches to access to highly fluorinated heteroatom-containing molecules have, for many elements, not been developed yet. To help put the situation into perspective, Figure 1 shows the accumulated fluorine-related publications of various elements.

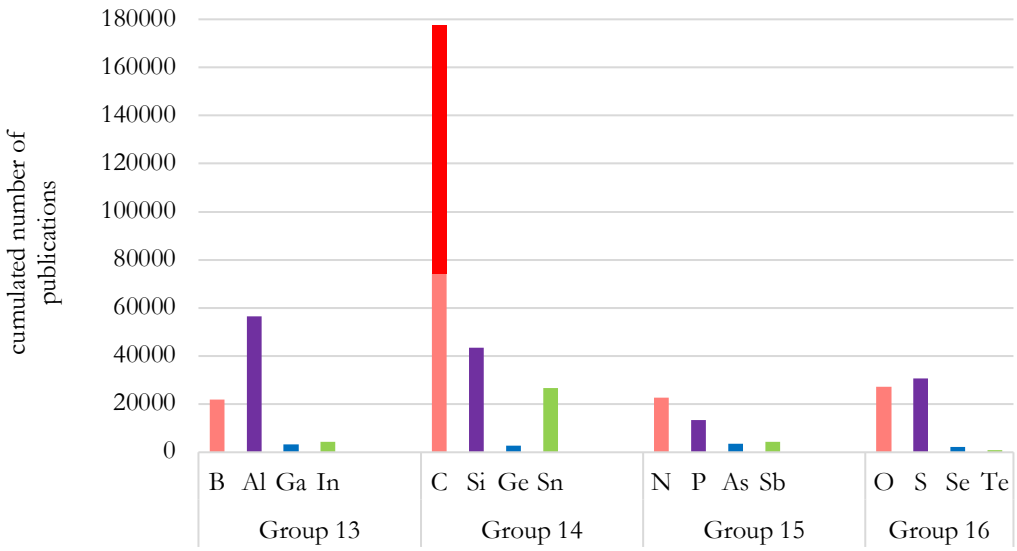


Figure 1: Cumulated references containing the concepts "fluorine/fluoride/fluoro + main group element" for elements of groups 13–16. In the case of carbon, the concept "trifluoromethyl" (dark red) was also included. Data extracted in August 2020 from the SciFinder® Database. Chemical Abstracts Service, USA.

It is obvious that the contributions to organofluorine chemistry with more than 170'000 publications far exceed those for any other main group element. Thus, the exploration of main group fluorine chemistry, the development of methodologies that allow facile access to fluorinated heteroatom species as well as the characterization of those compounds are problems still to be solved by modern 21st century fluorine chemists and represent, therefore, the focus of this thesis. The following chapters each focus on the fluorine chemistry of a specific element (i.e. sulfur, tellurium and phosphorus) and explore its historical development, modern synthetic applications and the author's contribution to the field in detail.

Chapter 2

Tetrafluoro-λ^6-sulfanyl Chlorides: Synthesis, Structural Investigations and Reactivity

Parts of this chapter are published and have been adapted with permission from:

«Making the SF_5 Group More Accessible: A Gas-Reagent-Free Approach to Aryl Tetrafluoro-λ^6-sulfanyl Chlorides» C. R. Pitts, **D. Bornemann**, P. Liebing, N. Santschi, A. Togni, *Angew. Chem. Int. Ed.* **2018**, *58*, 12604–12608; *Angew. Chem.* **2019**, *131*, 1970–1974. DOI: 10.1002/anie.201812356

2.1 Introduction

2.1.1 Sulfur – Historical Element

As one of the oldest known elements, sulfur occupies a very important position in human history. Mankind has known sulfur since prehistoric times and used it ever since.[18] Because the element occurs in nature with a relatively high abundance of 440 ppm in its native, solid, yellow S_8 form (Picture 2)[19] (in addition to numerous sulfur-containing compounds, i.e. pyrite, sulfates, etc.) it was easily accessible in a relatively pure form even in ancient times.[5] In fact, it was, alongside carbon, one of only two non-metals used by humans in the antiquity.[18] Archeologic findings in cave paintings and from preclassical Greece prove that the element was employed for a variety of tasks including the use for fumigation, in religious ceremonies, for cotton bleaching and more and is, as such, even mentioned in Homers *Odyssey*.[18,20,21] As mankind progressed through the ages, the applications of sulfur broadened. Pharmacists applied the element to treat a variety of skin diseases while alchemists discovered a more lucrative and impactful use for the chalcogen which, when mixed with potassium nitrate and charcoal, produces black powder.[20,22]

Picture 2: Crystalline sulfur, S_8. Found in Sicily, Italy.

In 1777, while the majority of the then still very young scientific community was under the impression that the coveted sulfur was a compound rather than an element, the French nobleman and "father of modern chemistry" himself, Antoine Lavoisier, took it upon himself to disprove that false hypothesis.[23] Together with Louis-Bernard Guyton de Morveau, Claude-Louis Berthollet, and Antoine François de Fourcroy, he coauthored the *Méthode de Nomenclature Chimique*, the first system of "modern" chemical nomenclature.[24] In their work, the scientists described a plethora of compounds that "[…] *could not be decomposed into simpler substances by any known chemical means* […]" and were consequently labeled *elements* and among those elements was also the chalcogen sulfur. Shortly thereafter, as the French revolution had begun to push the largely feudal, aristocratic Europe towards the industrialization era, the uses and demand of sulfur changed dramatically. Ritualistic uses had largely vanished and instead the production of black powder for wars and mining purposes and the growing metal, glass, textile, soap, and paper industries demanded an ever-increasing supply of sulfur or compounds thereof, most notably sulfuric acid.[25,26] Until 1880, he main source to feed the hunger for elemental sulfur had been deposits of volcanic soil in Sicily, which had thereby become the objects of desire of the leading European nations France and England.[25,27] The surging demand even culminated in a

famous trade conflict between the countries labeled "the Sulfur Crisis" in 1840, that could fortunately be resolved peacefully. The 1891 developed «Frasch process» marked a breakthrough in sulfur mining and allowed to satisfy the high demand for the element.[28] The process used superheated water that is pumped into an underground sulfur deposit, thus melting the chalcogen, which is finally pumped to the surface. The process was so successful that it remained the dominant sulfur mining method until 1971.[27] Only through the increased demand for energy and the resulting extensive mining for natural gas (and thereby also H_2S), chemical procedures like the "Claus process", which transform hydrogen sulfide into S_8, became more important and were able to gradually replace mining within the global sulfur production.[29] The demand, however, was still skyrocketing. While the global need for sulfur was about 10 million tons in 1971, the increasing demand has led to a production of elemental sulfur of 79 million tons in 2019.[27,30] Nowadays, sulfur is used for a variety of chemical processes. The prevalent use is the product of sulfuric acid (H_2SO_4), which is responsible for the consumption of 85–90% of the global sulfur production, which corresponds to a total annual production of sulfuric acid of more than 200 million tons.[31] A comparison to the Swiss catchment lake "Lago di Lei" (197 million tons of water at full capacity) helps to put this enormous amount into perspective. Other applications of the chalcogen include the synthesis of inorganic and organic sulfur compounds like SO_2, CS_2, P_2S_5, pharmaceuticals and more, making sulfur one of the chemical industry's most important raw materials.[18]

The rich history of sulfur combined with its manifold applications and its ready accessibility incentivized alchemists and later chemists to extensively study the element and its chemistry over the past centuries and millennia. As this thesis concentrates on the specific field of fluorinated heteroatom species, later subchapters (see 2.13) focus on a short overview of the most essential fluorine-containing sulfur compounds and related reactions in organic and inorganic chemistry. First though, to satisfy sheer curiosity, a characteristic and fundamentally interesting property of sulfur is quickly introduced, allotropism.

2.1.2 Sulfur Allotropy

As mentioned above, at standard conditions elemental sulfur is a yellow solid, which is typically described as being composed of S_8 rings (also frequently called S_α, Figure 2.[32] The ring size, however, is far from rigid and sulfur molecules of ring sizes S_n, $6 < n$

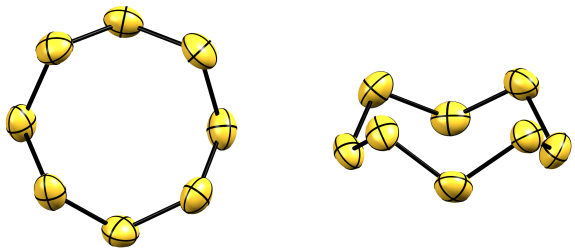


Figure 2: *ORTEP view* of yellow sulfur, S_8, as described by Hao *et al.* from a top view (**left**) and a side view (**right**) (displacement ellipsoids at 50% probability level). Co-crystallized molecules are omitted for clarity.

< 12 are easily formed upon melting of the solid, though there have been synthetic accounts for the existence of rings with up to n = 26 (Figure 3).[27,33,34]

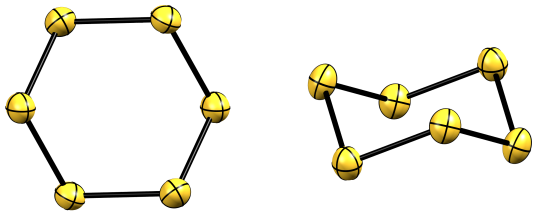


Figure 3: ORTEP view of S_6, measured by Fujiwara *et al.* (displacement ellipsoids at 50% probability level). Co-crystallized molecules omitted for clarity.

The property of an element to exist in two or more different forms, in the same physical state of matter is referred to as allotropism or allotropy (Greek: *allos* "other"). Other examples of allotropism are graphite and diamond in the case of carbon or white and red phosphorus. Sulfur is, behind carbon, the element with the second most known allotropic forms.[35] However, the typical S_8 rings are the most stable allotrope of sulfur and thus the most prevalent in the solid-state. The existence of rings with sizes S_n, n < 6 has been confirmed by mass spectrometry of sulfur vapors, but the smaller molecules contain very strained bonds, are thus very reactive and tend to polymerize easily.[27] Larger rings with n > 12 are unstable as they tend to eliminate more stable S_8 from their structure. Furthermore, they lack higher-order bond contributions, have unshielded atoms and are typically photosensitive as S–S bonds have, in analogy to O–O single bonds, low-lying triplet states, resulting in a rapid ring opening degradation of the formed chains.[27] The existence, synthetic accessibility and relative stability of rings with n > 12 have been investigated by Schmidt and Block.[36] They are typically formed in a reaction of linear HS_nH with ClS_mCl and form cyclic sulfur allotropes of the composition S_{m+n} with HCl as a byproduct.

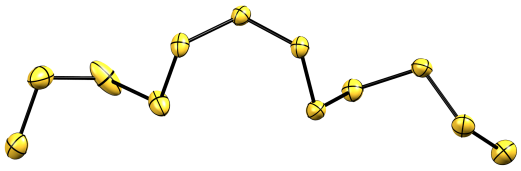


Figure 4: ORTEP view of S_{12}^{2-}, reported by Edelmann *et al.* (displacement ellipsoids at 50% probability level). Counterions omitted for clarity.

Apart from the typical ring allotropes, sulfur also exists in open chain-like structures, although neutral chains are expected to be diradicals and are thus rather reactive. However, the group of Edelmann has recently obtained in crystalline form the first open S_{12}^{2-} chain, as shown in Figure 4.[37] Other forms of sulfur allotropism can be found in a reordering of molecules within a crystal lattice (S_α is transformed into S_β upon heating without melting of the solid) and different prevalent allotropes in the liquid face at different temperatures (S_λ, S_π and S_μ).[18,27]

2.1.3 Sulfur Fluorine Chemistry – Remarks

As one of the oldest and most abundant elements known to mankind, numerous accounts on sulfur and related chemistry have been published since the dawn of modern science.

The formulation of a comprehensive and exhaustive overview of general sulfur chemistry is thus a feat hardly achievable within the scope of a doctoral thesis. A subset of sulfur compounds, however, is of particular interest for the chemistry described herein, sulfur fluorides. Thus, the next section will introduce sulfur fluorine chemistry with its most relevant compounds and emphasize the importance of the field.

2.1.4 High-Valent Sulfur Fluorides and Fluorohalides

Sulfur fluorides of all accessible positive oxidation states of the chalcogenide have been shown to exist.[18] Most known low-valent sulfur fluorides such as disulfur difluoride, thiothionyl fluoride and sulfur difluoride have no noteworthy applications to date and are, presumably due to their high reactivity and toxicity, rarely studied in contemporary chemistry. Two sulfur fluorides and their derivatives, however, are not only of interest for fundamental chemistry but are also used in large scale syntheses and found application in various industrial sectors. One of those is sulfur tetrafluoride, SF_4. Typically synthesized by fluorination of elemental sulfur (the synthesis also yields SF_6 and other sulfur fluorides) with fluorine gas, it is largely applied as a desoxyfluorination reagent, or in the synthesis of compounds used for the same purpose.[38,39] Handling of the toxic gas is challenging and thus multiple, less hazardous, liquid and solid derivatives of it have been synthesized. The chemistry of SF_4 and its derivatives is discussed in more detail in chapter 2.1.6.

The highest fluoride SF_6 is by far the most widely applied fluoride of sulfur and, as mentioned above, it is easily accessible by oxidative fluorination of S_8 with F_2.[18] The non-toxic and potent greenhouse gas is used in various industrial sectors, i.e. as a fire extinguishing agent, as a dielectric in high-voltage systems, as protective gas over molten metal, for thermal insulation, noise damping and more.[18] An interesting property of the gas is its remarkable chemical inertness. First noticed upon its initial synthesis by fluorine chemist Moissan, the compound is tasteless, inodorous, inert, thermally stable and, chemically speaking, resembles nitrogen much rather than SCl_6.[40] This unique inertness among the sulfur halides was also what inspired many chemists to investigate the hexafluoride in the upcoming decades after its discovery.

Other than the homoleptic hexafluoride, heteroleptic SF_5Cl and SF_5Br have been prepared, typically by oxidative addition of ClF or BrF to SF_4.[41–43] The heteroleptic derivatives are significantly less stable than SF_6 and are thus of high interest for the synthesis of SF_5-containing organic molecules.[44,45] Note that the introduction of the SF_5 moiety into an organic framework can dramatically affect its physical, chemical and biological properties, making the group fundamentally interesting for drug design, agrochemicals and life sciences in general.[46]

A whole subchapter is dedicated to SF_5 chemistry, its history, how it was developed and how molecular properties are affected by the group (subchapter 2.1.9.). Firstly, however, the applications of sulfur fluorides (SF_4 and SCF_3 species) in organic synthesis are introduced.

2.1.5 Sulfur-Based Reagents – Remarks

As introduced in chapter 1, the importance of fluorine in medicinal chemistry, agrochemistry, materials and more can hardly be overestimated. Installation of the element, however, requires well-established chemistry, producing suitable reagents that allow for selective and preferably mild, late-stage fluorination. When screening the available fluorination reagents, it quickly becomes apparent that a large number of them are sulfur-based and allow radical, electrophilic or nucleophilic fluorine transfer alike.[39] Due to the prevalence of sulfur in the named areas, the following subchapters will attempt to establish a brief overview of the development and application of the most widely used sulfur-based (desoxy)fluorination and fluoroalkylation reagents. The chapter does not claim to be comprehensive and should simply serve to emphasize the importance and actuality of sulfur fluorine chemistry. A more detailed, helpful review on that topic has recently been published by Hu and coworkers.[39]

2.1.6 Sulfur-Based (Desoxy)fluorination Reagents

Historically, the oldest nucleophilic sulfur-based desoxyfluorination reagent is SF_4. First discovered in 1928 by Fischer and Jaenckner the colorless gas initially gathered very little attention, likely due to its high toxicity, challenging synthesis and difficult handling.[47] It was first introduced as a desoxyfluorination reagent by Smith *et al.* in 1958/59.[48] In their publication the authors described a facile synthesis of the gas including the desoxyfluorination of various ketones and carboxylic acids, forming their corresponding difluoro- and trifluoro-derivatives. However, they also stated that the handling of SF_4 requires extreme care due to its fast hydrolysis and consequent formation of HF upon contact with moisture. Thus, it quickly became clear that in order to allow large scale and easy-to-handle sulfur-based desoxyfluorination, new, less hazardous reagents had to be developed.[49,50] The first commercialized desoxyfluorination reagents developed after SF_4, are the direct derivatives thereof, namely, *N,N*-diethylaminosulfur trifluoride (DAST) and bis(2-methoxyethyl)-aminosulfur trifluoride (Deoxo-Fluor®) (Figure 5).[51,52] Both reagents show high activity in the desoxyfluorination of compounds bearing hydroxyl and carbonyl oxygen atoms under mild conditions and with relatively facile procedures, as both are easy-to-handle liquids at room temperature.[39,51] However, especially DAST can undergo an explosive decomposition upon heating, making the compound potentially dangerous to use for larger-scale synthetic applications.[39,53,54]

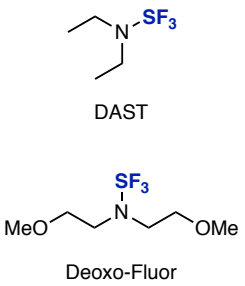


Figure 5: DAST (**top**), Deoxo-Fluor® (**bottom**).

A third generation of desoxygenative fluorination reagents was thus developed, including prominent compounds like (dialkylamino)difluorosulfonium tetrafluoroborates (XtalFluors®) and 4-*tert*-butyl-2,6-dimethylphenylsulfur trifluoride (Fluolead®).[55–57] These compounds are thermally stable solids, rendering them even more user-friendly and safe.

XtalFluors® are typically prepared by treatment of $TMSNEt_2$ with SF_4 and subsequent fluoride abstraction using BF_3·THF. The resulting salts are active in the desoxyfluorination of alcohols and carbonyl compounds and are more selective toward the fluorinated product with a decreased proportion of elimination side products formed.[57] However, due to the cationic nature of the sulfonium species, the reaction typically requires an additional fluoride source in the form of NEt_3·3HF species) or the addition of a base to produce a nucleophilic fluoride. [55,58,59]

In 2007 the Umemoto group reported the synthesis of 4-tert-butyl-2,6-dimethylphenylsulfur trifluoride, a compound they would later patent as Fluolead® (Figure 6).[56] Similar to DAST and Deoxo-Fluor® the compound is a neutral SF_4 derivative. Due to its larger organic framework, it is solid at room temperature and less prone to thermal decomposition.[39] Preparation of Fluolead® is achieved by direct chlorination to produce the aryl-SCl_3 derivative and subsequent chlorine–fluorine (Cl–F) exchange starting from the corresponding bis(4-tert-butyl-2,6-dimethylphenyl) disulfide using chlorine gas and KF.[56] The compound shows similar reactivity as other SF_4 derivatives.

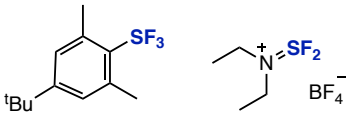


Figure 6: Fluolead® (**left**), XtalFluor-E® (**right**).

The advent of non-gaseous desoxyfluorination reagents has thus opened the possibility to prepare an array of organic fluorides from easily-accessible oxygen-containing starting materials.

2.1.7 Sulfur-Based Trifluoromethylation Reagents

Next to desoxyfluorination, the development of fluoroalkylation reagents has made a significant leap within the last three decades. Analogous to fluorine itself, the trifluoromethyl group (CF_3) has gained widespread attention in the fields of pharmaceutical chemistry, agrochemistry, materials and more.[39,45,46,60,61] Apart from iodine-based trifluoromethylation reagents, developed in our group, again a large number of said reagents are sulfur-based.[39,62] A short overview of the prevalent reagents for these transformations is given in this section.

Two compound classes that are used in trifluoromethylation reactions are sulfoxides and sulfones, and both are generally prepared by oxidation of the corresponding thioethers (Figure 7).[63–65] In 2003 the group of Prakash had found that $PhSOCF_3$ or $PhSO_2CF_3$ in combination with KO*t*Bu are well suited for nucleophilic trifluoromethylations of carbonyl compounds.[66] Furthermore, upon reaction with magnesium metal, the compounds act as electron acceptors thereby generating the trifluoromethyl anion (CF_3^-). Based on this reactivity the Prakash group prepared the now-famous Ruppert-Prakash reagent $SiMe_3CF_3$ ($TMSCF_3$) from TMSCl. Although sulfones and sulfoxides can also be used in radical trifluoromethylation reactions, this direction is significantly less developed in comparison to their application in nucleophilic trifluoromethylations.[67–70]

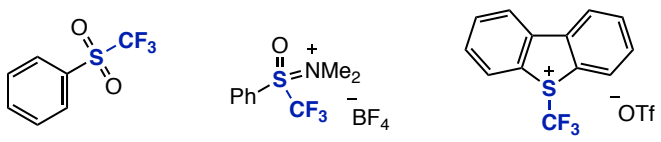


Figure 7: Selection of the predominantly used sulfur-based trifluoromethylation reagents.

Another sulfur-based compound class for trifluoromethylation reactions is composed of sulfoximines. Whereas sulfones and sulfoxides are mainly applied for nucleophilic trifluoromethylation, sulfoximines are frequently used in electrophilic trifluoromethylation reactions.[39] Synthesis is typically achieved through oxidative imination of the corresponding sulfoxides and subsequent *N*-functionalization.[71–74] The first electrophilic trifluoromethylation with sulfoximine salts was reported in 2008 by Shibata and coworkers.[74] The group used *N*,*N*-dimethyl-*S*-trifluoromethylsulfoximinium tetrafluoroborate together with DBU or other organic bases for the trifluoromethylation of β-keto esters and other carbon nucleophiles. The methodology could even be extended to allow trifluoromethylation of alkynyl lithium species.

The perhaps oldest and most widely used sulfur-based electrophilic trifluoromethylation reagents are centered around sulfonium salts.[39] Their first appearance in the literature as CF_3 transfer reagents dates back to 1984.[71] Kondratenko *et al.* described the synthesis of a trifluoromethyl(diaryl)sulfonium hexafluoroantimonate species that facilitates access to trifluoromethylated thioethers from organic thiolates. The used sulfonium salts were rather unreactive and it was not until 1990 when Umemoto and Ishihara were able to improve the concept by accessing S-heterocyclic sulfonium salts.[75] Derivatives of their initial scaffold are now widely used for the trifluoromethylation of arenes, alkenes, terminal alkynes, ketoesters and more and are commercially available as Umemoto reagents.[76]

Other than sulfur-based perfluoroalkylation reagents, a variety of difluoromethylation and fluoromethylation reactions have been developed recently but are, in the context of this thesis, of secondary interest. The same holds for transition metal-mediated fluorine or trifluoromethyl transfer reactions. For further reading on this topic, the comprehensive review by Hu and coworkers is recommended again.[39]

2.1.8 The Pentafluorosulfanyl Group – SF_5

Alongside the use of sulfur-based reagents for trifluoromethylation or fluorination, another branch of sulfur fluorine chemistry has grown over the past decades. The focus therein lies on the use of fluorinated sulfur, not as a reagent, but as a functional group. Within this particular area, one highly interesting functional group stands out, i.e. pentafluorosulfanyl or SF_5. Since a large portion of the knowledge gained in this chapter is related to aryl-SF_5 compounds, a short introduction to aryl-SF_5 chemistry is given below. The main focus is on the properties and syntheses of these SF_5 substituted organic compounds and the development of the methods that enabled their synthetic access in the course of history. Comprehensive reviews have been published recently by Savoie and Altomonte.[45,77]

2.1.9 Physicochemical Properties of SF_5

As previously discussed, the most widely used sulfur fluoride is SF_6 gas.[18] The discovery that the hexafluoride is extraordinarily stable, especially when compared to its lower-valent congeners like SF_4 (and S_2F_{10}), inspired the development of a range of SF_6 derivatives, most notably organic RSF_5 compounds. As mentioned above, the introduction of SF_5 into an organic molecule affects the properties of the latter to a large extent. This effect is due to the unique stereoelectronic and geometric properties of the pentafluorosulfanyl group.[45] In the past, various authors have repeatedly drawn comparisons between the SF_5 and the CF_3 groups.[45,77,78] Similar to CF_3, SF_5 shows remarkable chemical stability, and so the group is not prone to hydrolysis, nucleophilic attacks or reductions and shows a high inertness towards Brønsted acids and bases alike.[45] Furthermore, both compounds share a highly fluorinated surface and relatively high electronegativity with SF_5 assuming a value of 3.65 and CF_3 having a slightly lower electronegativity of 3.36.[79]

The Hammett parameters of both groups were also determined and compared. Again, they show high similarity, with the SF_5 group (σ_p = 0.68, σ_I = 0.55 and σ_R = 0.11) having comparable or slightly larger values than its CF_3 equivalent (σ_p = 0.54, σ_I = 0.39 and σ_R = 0.12).[80–82] Recently, because of these striking similarities and since SF_5 typically leads to enhanced lipophilicity, the nickname "super CF_3" was coined for the pentafluorosulfanyl group.[78] Resemblances aside, both groups also have distinct differences that define how a molecule is affected by their introduction. One of those key differences are their structural features. Whereas CF_3 adopts a tetrahedral structure around the central carbon atom, SF_5 is octahedral, a geometry rarely seen for a substituent in organic molecules (Figure 8). As Welch and coworkers mentioned, this rather unusual geometry of a substituent and the low rotational barrier of the C–S bond render the group an excellent candidate for ligand–receptor interaction optimizations.[45] Another noteworthy difference between the trifluoromethyl and pentafluorosulfanyl groups is their relative steric bulk.

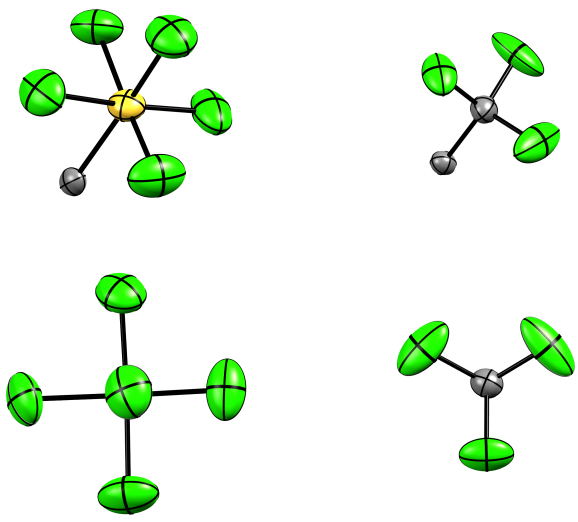


Figure 8: **left**: octahedral C(sp^2)-SF_5 fragment from side and top view,
right: tetrahedral C(sp^2)-CF_3 fragment from side and top view.
Displacement ellipsoids at 50% probability level.

The SF_5 group is a sterically highly demanding group with 1.3–1.5 times the volume of a CF_3 group, making it more comparable in size to a *tert*-butyl substituent, however, again with distinctly different geometries and electronic properties.[83,84]

Due to the largely similar electronic properties of SF_5 and CF_3 and their key differences in size and geometry together with the long-established use of CF_3 in medicinal chemistry, agrochemistry, material sciences and more, various research groups have propagated the synthesis and application of SF_5-bearing organic analogues to already known CF_3 counterparts.[45,77] As a consequence, various SF_5 substituted variants of existing and applied CF_3-containing drugs and agrochemicals including Mefloquine (anti-malarial),[85] Norfenfluramine (serotonin uptake inhibitor),[46] Fipronil (insecticide)[86] and Trifluralin (herbicide)[87] have been synthesized and, in part, have demonstrated advantageous properties over their CF_3 equivalents, showing the latent potential of the highly fluorinated substituent. Yet, despite this enormous potential of the SF_5 group for the life sciences and chemical industry, the group and its properties remain considerably underexplored in comparison to the CF_3 group. A plausible explanation for this finding is the difficult synthetic access to SF_5-bearing molecules compared to the well-established trifluoromethylation protocols found in the literature. The next subchapters will examine the existing synthetic routes to aryl-SF_5 species, their development over time and their limitations.

2.1.10 Aryl-SF_5 in the Course of History

Even though the interest in aryl-SF_5 chemistry remained high after the initial discovery of the pentafluorosulfanyl group, the development of chemistry facilitating the access to SF_5-substituted arenes has been considerably slow. Since the advent of aryl-SF_5 chemistry, four key developments in the synthesis of aryl-SF_5 compounds can be identified. In an attempt to summarize those most important developments, the timeline displayed in Figure 9 was generated and should serve as a reference point for the reader.

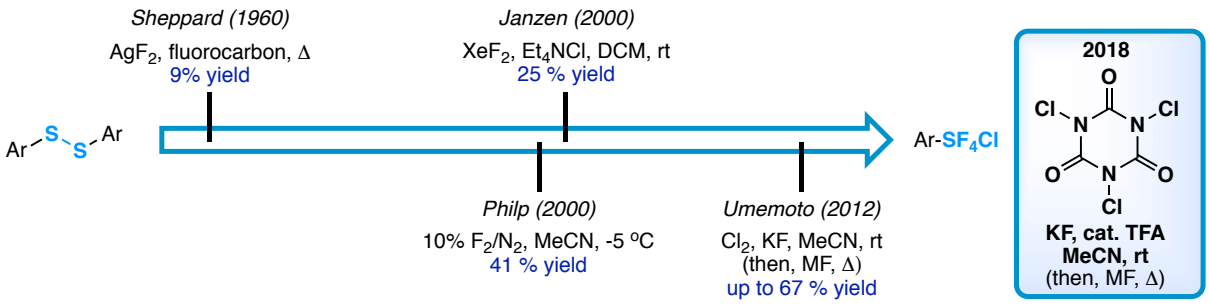


Figure 9: Timeline with the most important developments in aryl-SF_5 chemistry.

2.1.11 Developments in the Synthetic Accessibility of Aryl-SF_5 Species

While the first synthesis of an organic SF_5 derivative was published in 1950 by Silvey and Cady, who treated MeSH or CS_2 with CoF_3 at 200°C affording CF_3SF_5 as a colorless gas in up to 40% yield, it was not until 10 years later when aromatic SF_5 derivatives were first described.[88] The earliest report of pentafluorosulfanylated arenes dates back to 1960. Sheppard treated diaryl disulfide (Ar_2S_2, Ar = Ph, *meta*- or *para*-NO_2-Ph , *meta*- or *para*-CH_3-Ph) in the fluorocarbon solvent CFC-113 with AgF_2 in an oxidative fluorination reaction.[89] The conditions primarily afforded aryl-SF_3 and only after prolonged heating to 130°C in a sealed copper or Teflon vessel low yields (9 – 30%) of aryl-SF_5 could be obtained. The compounds were analyzed by NMR, UV and IR spectroscopy and Sheppard was able to confirm the remarkable chemical inertness of SF_5 comparing it to trifluorotoluene in terms of hydrolytic and thermal stability. Furthermore, the author conducted the first derivatization experiments on the newly obtained aryl-SF_5 compounds. The nitro-substituted derivatives were subjected to reductive hydrogenation, affording the corresponding anilines without degradation of the SF_5 group. These products were in turn acetylated and diazotized (although exact methods and yields are not given). While only a few examples of aryl-SF_5 species were obtained in relatively poor yields in this work from 1960, this report, nevertheless, marked the origin of aryl-SF_5 chemistry.

Following this initial discovery by Sheppard, many new aryl-SF_5 compounds were synthesized using his method. Unfortunately, however, the poor yields obtainable with these conditions could not be significantly improved, rendering the synthesis of pentafluorosulfanylated arenes unrewarding and expensive.[90–92]

It took nearly 40 years before the group of Philp focused on the oxidative fluorination of disulfides with fluorine gas in 2000. The authors describe the synthesis of (4-nitrophenyl)sulfurpentafluoride in 41% and (3-nitrophenyl)sulfurpentafluoride in 39% yield by treatment of their corresponding disulfide starting materials with F_2/N_2 (1:9) in MeCN at -5°C.[93] Other than a facilitated synthetic route to aryl-SF_5 compounds the group also report how the obtained nitro-derivatives can be used as starting materials for derivatization reactions. Therefore, they started with the reduction of the nitro group with H_2 and palladium on carbon as already described by Sheppard. The resulting anilines were obtained in 70% yield for the *meta*-derivative and 48% yield for the *para*-compound.

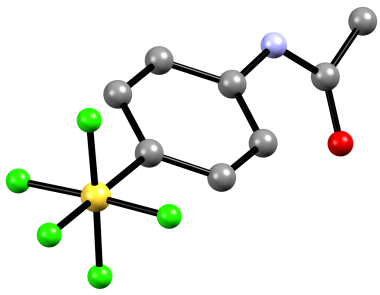


Figure 10: First crystal structure of an aryl-SF_5 compounds as reported by Philp. No illustration with thermal ellipsoids was available.

The anilines were acetylated in subsequent reactions in a manner analogous to Sheppard's work and a yield of 37% and 42%, respectively, was obtained. Furthermore, the first crystal structure of an aryl-SF_5 compound was reported (Figure 10). More interestingly, the synthesis of (3- and (4-iodophenyl)sulfurpentafluoride by diazotization of the anilines with $NaNO_2$ and HCl and subsequent iodination with KI (in 50–63% yield) was also described. This newly obtained aryl-SF_5 compound was then proven to be a suitable substrate in cross-coupling reactions (Suzuki and Stille coupling), affording the more complex alkynyl, alkenyl and phenyl derivatives. The newly found possibility to use aryl-SF_5 compounds as building blocks in cross-coupling reactions certainly paved the way for a broader application of the functional group in an industrial setting.

In the same year as Philp and coworkers developed their oxidative fluorination of diaryl disulfides with F_2/N_2, Janzen and coworkers showed that XeF_2 can be used as a suitable replacement for AgF_2 in the synthesis of pentafluorosulfanylated arenes from diaryl disulfides in DCM at room temperature.[94] Upon the addition of XeF_2 to the disulfide, aryl-SF_3 is formed within 24 h and in good yields (60–90%). However, the reaction does not yield aryl-SF_5 derivatives without the addition of catalytic amounts of NEt_4Cl (compare also chapter 3, $PhTeF_5$). Under catalytic conditions, the target compounds can be isolated with up to 25% yield. While the potential to move away from highly hazardous and toxic fluorine gas justifies the use of solid XeF_2 as a surrogate, the method still suffers from crippling disadvantages compared to the previous methods. The yields of the obtained aryl-SF_5 species are very low and XeF_2 is a very expensive, potentially explosive fluorinating regent, both problematic features that drastically limit the utility of the method.

Arguably the most significant advancement in the synthesis of aryl-SF_5 compounds is the two-step route reported by Umemoto in 2012.[95] Instead of direct fluorination of disulfide starting materials, the method generates a new avenue via intermediary formation of a key aryl tetrafluoro-λ^6-sulfanyl chloride (aryl-SF_4Cl) intermediate. To this end Umemoto and coworkers developed a two-step procedure, first treating diaryl disulfides with excess chlorine gas and potassium or cesium fluoride in MeCN at room temperature. This affords the corresponding aryl-SF_4Cl derivatives in good to excellent (60–97%) yields. In order to obtain aryl-SF_5 species from their SF_4Cl counterparts, a second step in the form of a Cl–F exchange reaction has to be carried out. Umemoto found that this subsequent halide exchange works best by the reaction of the neat aryl-SF_4Cl with ZnF_2 at 80°C for 24 h, affording the corresponding aryl-SF_5 derivatives in up to 85% yield. Other fluorination reagents like HF, SnF_4, TiF_4, SbF_3 or SbF_5 and more were also successively applied to afford pentafluorosulfanyl species in slightly lower yields. Methods to achieve halide exchange have since been further improved in the groups of Dolbier (e.g. AgF, neat, 60°C, 16 h)[96],

Shibata (e.g. IF_5, neat, 65°C, 14 h)[97] and Beier (KHF_2, TFA, rt, 12–20 h).[98] Umemoto's method allowed for the synthesis of a library of differently functionalized aryl-SF_4Cl compounds, including halide-, nitro-, trifluoromethyl-substituted arenes and more. Another key advantage of the methodology was that, using the obtained SF_4Cl species, chemistry beyond aryl-SF_5 was conceivable. An example of such chemistry was provided by Welch and coworkers who described the synthesis of aryl-SF_4R (R = alkenyl moiety) compounds from their SF_4Cl derivatives, by activation of the latter with the radical initiator triethyl borane and subsequent reaction with alkynes.[99] Chemical limitations of Umemoto's method were mainly related to functional group tolerance and electronic properties of the applied arenes. Explicitly, the method was only applicable to electron-poor or -neutral arenes, substituted with functional groups that tolerate the strongly oxidizing conditions that an atmosphere of chlorine gas provides. Noteworthy, electron-donating substituents like alkyl, methoxy, or amino groups render the aromatic ring too electron rich, which can lead to competitive ring chlorination reactions and are thus also a limiting factor for the method. These shortcomings hamper late-stage functionalization of many intermediates which could be of interest for applications in the life sciences, but are not robust enough to withstand Cl_2. Nevertheless, the Cl_2/KF method revolutionized the field as, for the first time, access to aryl-SF_5 species was possible without the application of extremely hazardous fluorine gas or expensive fluorides like AgF_2 or XeF_2. This development allowed for drastically lower production and selling prices for aryl-SF_5 molecules and thus made them much more accessible, significantly facilitating their application as starting materials and building blocks for synthetic applications.

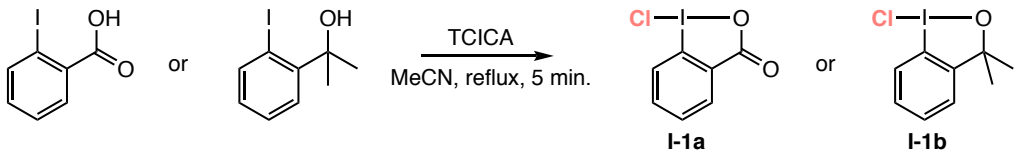
However, like the previous methods, Umemoto's Cl_2/KF protocol still suffers from a major, handling related, drawback. As much as the exchange of F_2 gas for Cl_2 has improved the user-friendliness of the reactions towards aryl-SF_5 species, chlorine remains a difficult-to-handle, highly toxic, corrosive gas. Thus, at least in an academic setting, many laboratories and chemists may not have the infrastructure, know-how or equipment for safe, controlled use of such chemicals. It, therefore, seems logical that the next step towards easily accessible SF_5 chemistry should be the complete avoidance of gaseous reagents. A first part of this thesis was devoted to the exploration of reactions that might allow to finally tackle this synthetic Achilles' heel in the development of aryl-SF_5 chemistry. The results of this *Odyssey* in organosulfur fluorine chemistry are described in the next sections.

2.2 Results and Discussion

2.2.1 Introductory Remarks

In light of the limited availability of easy-to-use methods to generate SF_5 substituted molecules, we tackled the main problem in the synthesis of these compounds, i.e. the use of expensive chemicals and/or highly toxic, corrosive gases. We were guided in our research by Umemoto's results for the production of aryl-SF_4Cl compounds and their subsequent conversion to SF_5 derivatives by Cl–F exchange. Since, as described above, the second step of this well-known method had already been thoroughly investigated and optimized, we concentrated on the first step, the oxidative chlorofluorination. So, the question at hand became: *Can we replace Cl_2 with a preferably solid, easy-to-handle oxidative chlorination reagent, without losing the efficacy, tolerance and rather high yields achievable with chlorine?*

Inspiration for an answer to this question came from a reaction that was regularly performed in our group. The oxidative chlorination of aryl-iodine compounds en route to iodine-based trifluoromethylation reagents. In 2013 Matoušek *et al.* published the application of trichloroisocyanuric acid (TCICA) for the oxidative chlorination of 2-iodobenzoic acid and 2-(2-iodophenyl)propan-2-ol to form their corresponding chloroiodanes **I–1a** and **I–1b** (Scheme 1).[100] TCICA is a bench-stable, non-hygroscopic, very easy-to-handle colorless solid, which is frequently used as swimming pool disinfectant and in addition to its comparatively low toxicity also extremely cheap, thereby making it an ideal candidate for the replacement of chlorine gas.



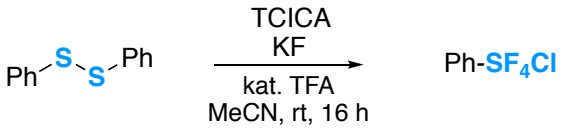
Scheme 1: Oxidative chlorination of aryl-iodine compounds with TCICA as reported by Matoušek *et al.*

With this knowledge at hand and Umemoto's method in mind, we went on to carry out a first reaction of diaryl disulfides with TCICA and spray-dried KF under a nitrogen atmosphere. In our first attempt, unfortunately, $PhSF_4Cl$ was not formed in a significant amount but instead incomplete conversion to $PhSF_3$ occurred. In a subsequent attempt, catalytic (0.1 equiv.) trifluoroacetic acid (TFA) was added to the reaction mixture. After analysis of the reaction mixture, we were pleased to find that treatment of diphenyl disulfide (**S-1a**) with TCICA/KF and catalytic TFA indeed yielded *trans*-$PhSF_4Cl$ in significant yields (see Table 1 below).

These newly found promising initial reaction conditions were subsequently optimized and tested by screening for TCICA and KF equivalents, solvents, additives, temperatures, reaction times and the application of alternative oxidants. This procedure generated the data summarized below in Table 1. The full screening table can be found in the appendix.

2.2.2 Screening

Table 1: Abbreviated screening for the synthesis of $PhSF_4Cl$ with TCICA/KF.



entry	*TCICA (equiv.)*	*KF (equiv.)*	*yield (%)*	*notes*
1	9	16	0%	-
2	18	32	47%	0.5 equiv. TFA
3	27	48	trace	0.5 equiv. TFA
4	9	16	0%	0.5 equiv. TFA, in $MeNO_2$
5	9	16	21%	0.5 equiv. TFA, in EtOAc
6	9	16	48%	0.1 equiv. TFA
7	9	16	0%	0.5 equiv. $FeCl_3$
8	9	16	21%	0.5 equiv. CuCl
9	**18**	**32**	**70%**	**0.1 equiv. TFA**
10	18	32	65%	0.1 equiv. $ZnCl_2$
11	18*	32	0%	*used NCS
12	18*	32	0%	*used N-chloro-phthalimide

^{19}F NMR yield reported.

The reactions were carried out in non-deuterated solvents and monitored by ^{19}F NMR, therefore yields given in Table 1 are ^{19}F NMR yields. Evaluation of the screening data showed that best yields of $PhSF_4Cl$ were obtained when 18 equiv. TCICA and 32 equiv. KF were used. The ratio of TCICA:KF is vital to obtain optimal yields, as shifting it in favor of the former can increase the formation of byproducts deriving from putative ring chlorination. It is noteworthy that frequently observed byproducts which do not stem from ring chlorination and often constitute the majority of the mass balance are not fully converted $PhSF_3$ or the hydrolysis product $PhSOF_3$ (and to a minor extent $PhSO_2F$ and PhSOF). It is thus important for the applied fluoride sources (here KF), additives and solvents to be rigorously dried (preferably spray-dried or distilled) in order to minimize byproduct formation. Screening of different additives revealed that the addition of catalytic amounts of acid is essential to obtain reproducibly high yields. We screened Lewis and Brønsted acids alike, generating best yields with TFA and $ZnCl_2$, whereas other metal salts

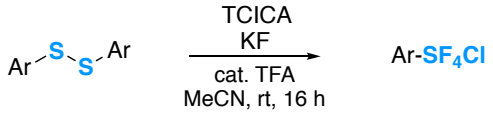
like CuCl result in a significantly lower or, like in the case for $FeCl_3$, no detectable yield at all. Here, the use of liquid TFA rather than $ZnCl_2$ or other metal salts is preferred simply for reasons of practicality. Note, the application of stoichiometric quantities or excess TFA instead of catalytic amounts will partially or completely inhibit $PhSF_4Cl$ formation and should thus be avoided. Upon identification of the most suitable additives, we tried to replace TCICA with other oxidants that are known to function as formal Cl^+ sources, specifically N-chlorosuccinimide (NCS) and N-chlorophthalimide (NPhth). Astonishingly, neither NCS or NCPhth are suitable replacements for TCICA. Not only did neither reagent yield any $PhSF_4Cl$, but even the formation of S(IV) fluorides couldn't be observed in these cases. When focusing on the solvent, best results were obtained with MeCN, similarly as with Umemoto's method. The use of $MeNO_2$ or EtOAc led to strongly reduced product formation instead. Noteworthy, background aromatic ring chlorination occurs when heating the reaction mixture to 40–50°C. Finally, other than disulfides it is also possible to employ arylsulfenyl chlorides (aryl-SCl compounds) as starting materials for aryl-SF_4Cl synthesis.

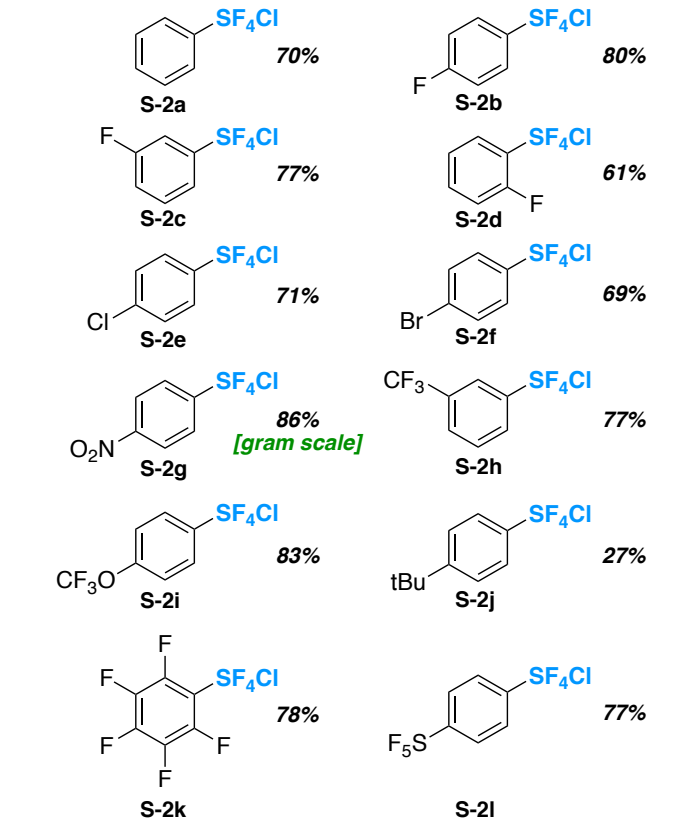
To conclude the screening, it was determined that highest ^{19}F NMR yields of 70% $PhSF_5$ can be obtained by stirring Ph_2S_2 with 18 equiv. TCICA, 32 equiv. KF and 10 mol% TFA in MeCN overnight at room temperature.

2.2.3 Synthesis and Characterization of Tetrafluoro-λ⁶-sulfanyl Chlorides

With the newly found, optimized reaction conditions in hand, it was possible to investigate not only the scope of the reaction but also its limitations (Table 2). Therefore, it was attempted to reproduce the synthesis of previously accessed aryl-SF_4Cl species by Umemoto's method using the TCICA/KF approach instead. In analogy to the Cl_2/KF method, we found that the reaction works best with electron-poor or electron-neutral arenes. Mildly to strongly electron-withdrawing groups like halido- (**S-2b-f**, **S-2k**), nitro- (**S-2g**) or trifluoromethyl- (**S-2h**) trifluoromethoxy- (**S2-i**) and pentafluorosulfanyl-substituents (**S-2k**) are well tolerated and all allow for the formation of the desired aryl-SF_4Cl compounds in good yields. More problematic are electron-donating functional groups. As previously reported, electron-rich arenes tend to undergo ring chlorination reactions when subjected to an atmosphere of chlorine gas.[95] This observation can also be made when using TCICA, which unfortunately excludes electron-donating substituents in connection with this methodology.[101] This also holds true for the use of a *tert*-butyl substituted entry (**S-2j**), which, even though it prevents alpha chlorination and sterically inhibits ring chlorination, only gave the desired aryl-SF_4Cl species in a low 27% yield. In addition, it did not seem to matter in terms of yield whether the arenes had a *para*- or *meta*-substitution pattern. However, it is noteworthy that no or only small substituents like fluorine atoms can be placed in the *ortho* positions, since larger substituents are likely to act as steric barriers to prevent the formation of aryl-SF_4Cl. On another note, we observed an interesting behavior, analogous to Umemoto's observations, that showed preferential, or in some cases exclusive formation of *trans*-aryl-SF_4Cl. Only few compounds are exceptions to this rule, like **S-2k**, (and **S-2z**, *vide infra*) in which case the ratio of *trans* to *cis* isomer is about 1.5:1. We could not find a definite explanation for the occurrence of

Table 2: Scope of known aryl-SF_4Cl species reproduced using the TCICA/KF approach.



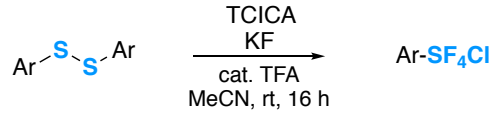


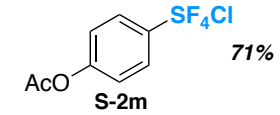
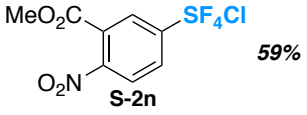
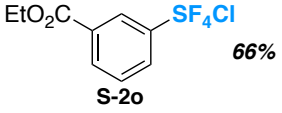
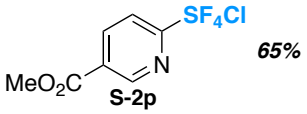
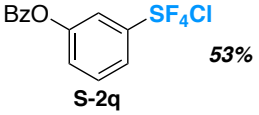
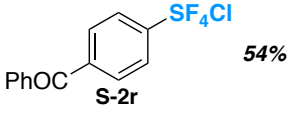
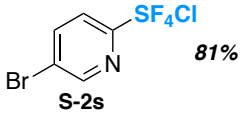
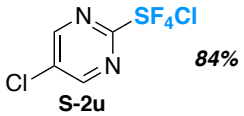
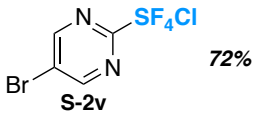
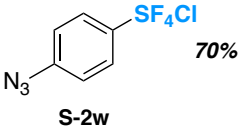
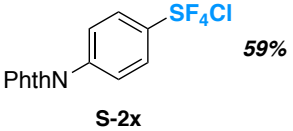
[19]F NMR yields.

those differences in isomeric ratios within our studies. Note that the reactions were typically carried out on a 100–200 mg scale but as shown for entry **S-2g** can also be performed on a multigram scale (here 2 g) with no decrease in yield. On the contrary, upscaling the quantity of disulfide allows a reduction of the amounts of TCICA and KF to 12 equiv. and 20 equiv. respectively, which is comparable to the results published by Umemoto.

While it is possible to circumvent the use of Cl_2 and to produce an array of previously known aryl-SF_4Cl species with our new TCICA/KF method, we were also able to access a number of heretofore unknown aryl-SF_4Cl compounds, thus greatly increasing the scope of our methodology. Here, the possibility to access various products containing ester- (**S-2m-q**), ketone- (**S-2r**), and nitrogen-containing substituents, (e.g. azide, **S-2w** or phthalimide, **S-2x**) is a noteworthy improvement (Table 3). Additionally, nicotinic acid derivative **S-2p** demonstrates the compatibility of ester-containing heteroaromatic substrates. Other substituted pyridine and pyrimidine heteroaryl-SF_4Cl derivatives have been reported independently by Dolbier[96] and Shibata[97] using the Cl_2/KF method. We have also found that our TCICA/KF approach offers access to similar compounds in good yields (i.e. **S-2s-v**).

Table 3: Scope of new (hetero)aryl-SF_4Cl species accessible using the TCICA/KF approach.

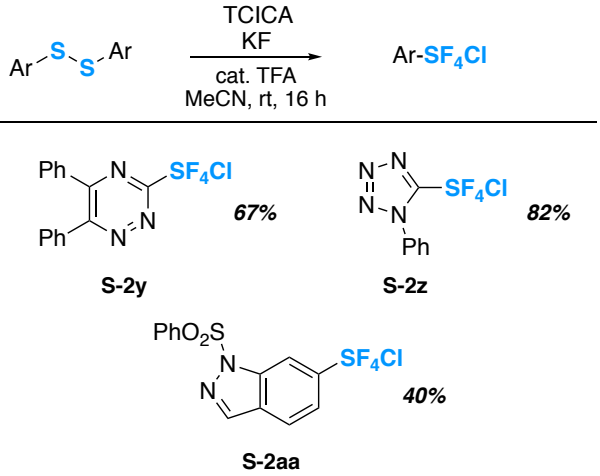


 **S-2m** *71%*	 **S-2n** *59%*
 **S-2o** *66%*	 **S-2p** *65%*
 **S-2q** *53%*	 **S-2r** *54%*
 **S-2s** *81%*	 **S-2t** *62%*
 **S-2u** *84%*	 **S-2v** *72%*
 **S-2w** *70%*	 **S-2x** *59%*

[19]F NMR yields.

The most notable deviation from previously reported aryl-SF_4Cl compounds are found in the accessibility of novel heteroaryl-SF_4Cl derivatives, such as triazine **S-2y**, tetrazole **S-2z**, and indazole **S-2aa** via the TCICA/KF approach (Table 4). Compound **S-2z** represents a notable departure from six-membered ring-based substrates and, as the only entry among all herein accessed SF_4Cl species, interestingly favors the *cis*- over the *trans* isomer (2.9:1 *cis*:*trans*). Furthermore, **S-2aa** is a rare example of a benzo-fused heteroaryl-SF_4Cl compound, highlighting the potential to install the SF_5 group onto more complex heteroaromatics that are otherwise accessible using building block approaches only.[102]

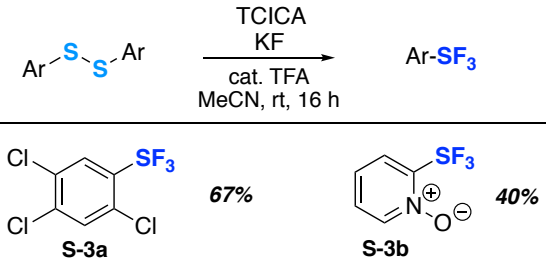
Table 4: Scope of new classes of heteroaryl-SF_4Cl species accessible using the TCICA/KF approach.



^{19}F NMR yields.

As previously mentioned, aryl-SF_4Cl formation is inhibited by the presence of ortho substituents larger than hydrogen or fluorine atoms. In such cases, we noted that instead of reaching the S(VI) oxidation state, we observed excellent yields of compounds in the S(IV) oxidation state, that is, aryl-SF_3 products **S-3a** and **S-3b** (Table 5). As discussed above other aryl-SF_3 compounds, such as Fluolead® or mesitylsulfur trifluoride, may be applied as desoxyfluorination reagents, and are typically prepared using the Cl_2/KF method.[56] Although we haven't investigated their reactivity as such reagents yet, the TCICA/KF approach could allow other research groups to further develop aryl-SF_3 chemistry without having to rely on the use of chlorine gas.

Table 5: Scope of new of (hetero)aryl-SF_3 species accessible using the TCICA/KF approach.



^{19}F NMR yields.

In all cases, the previously unknown, newly synthesized aryl-SF_4Cl species were isolated from their TCICA/KF reaction mixture by extraction with hexane:DCM (9:1) and subsequent solvent removal. Especially interesting was their behavior in ^{19}F NMR spectroscopy, which is shortly discussed in the following subchapter.

2.2.4 NMR Spectroscopic Characterization of Aryl-SF_4Cl Derivatives

As discussed previously, analyzing the structure of aryl-SF_4Cl compounds, one can identify two potential isomers for this compound class, *trans*- and *cis*-aryl-SF_4Cl. In most cases, the *trans* isomer is formed exclusively, with all fluorine atoms being chemically equivalent in the equatorial positions around the sulfur central atom. This arrangement results in rather simple ^{19}F NMR spectra, as the equivalent fluorine atoms result in a single, sharp singlet. In order to allow a more intuitive understanding of the ^{19}F NMR chemical shifts displayed by these compounds, an average with standard deviation of all ^{19}F NMR shifts for compounds of the **S-2** series was calculated from spectra collected under the same conditions (MeCN-d_3, room temperature). The average chemical shift is 133.46 ± 6.76 ppm, with the lowest shift being 118.97 ppm for compound **S-2v** and the highest 143.21 ppm for compound **S-2k**. The only two species showing significant fraction of the corresponding *cis*-aryl-SF_4Cl species are **S-2k** and **S-2z**. As mentioned above in these cases the ratio of *cis*:*trans* was 1:1.5 and 2.9:1, respectively. Here, the ^{19}F NMR spectra become more complex as depicted in Figure 11. Instead of only one set of signals for four equivalent F-atoms, the compounds exhibit three different sets, for the three now inequivalent sets of fluorine atoms. As an example, the shifts of **S-2z** are given here: +146.30–144.99 ppm (1F, m), +117.03 ppm (2F, dd, ^2J = 163.5, 96.8 Hz) and +76.73 ppm (1F, dt, ^2J = 163.5, 96.8 Hz).

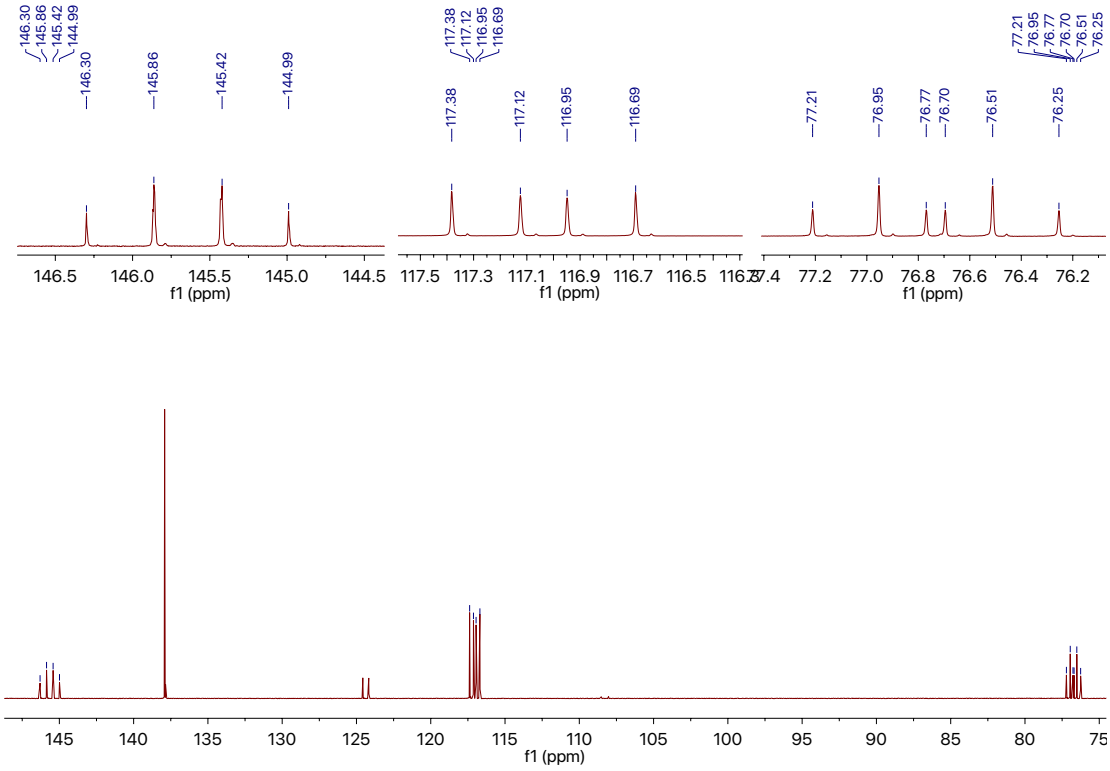


Figure 11: ^{19}F NMR spectrum of **S-2z**. Enlarged signals belong to the *cis*-SF_4Cl group. Also prominent is the singlet at ca. 138 ppm belonging to the *trans*-SF_4Cl species.

2.2.5 Solid State Analysis of a Representative Aryl-SF_4Cl Derivative

Despite the work of multiple research groups in the field of aryl-SF_4Cl chemistry, no solid-state data was available when we began working on the TCICA/KF approach. As SF_4Cl species tend to slowly undergo hydrolysis when subjected to moisture (i.e. atmospheric water) crystallization attempts have to be conducted under the rigorous exclusion of water. We opted for crystallization in a glovebox to avoid any decomposition. Fortunately, by slow evaporation of a solution in DCM:*n*-hexane (1:10), we were able to obtain crystals suitable for X-ray diffraction of a compound containing a biaryl scaffold that is, however, not listed in the tables above as it was never isolated due to its poor solubility, namely **S-2ab** (Figure 12).

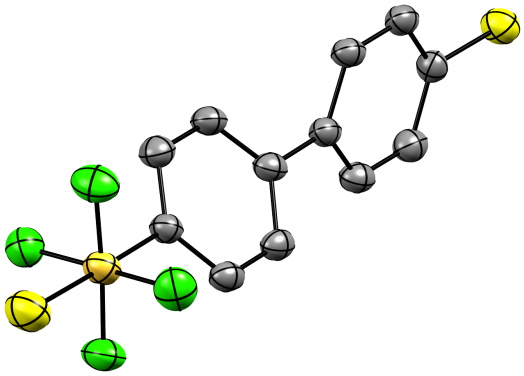


Figure 12: ORTEP view of **S-2ab** (displacement ellipsoids at 50% probability level). Hydrogen atoms omitted for clarity.

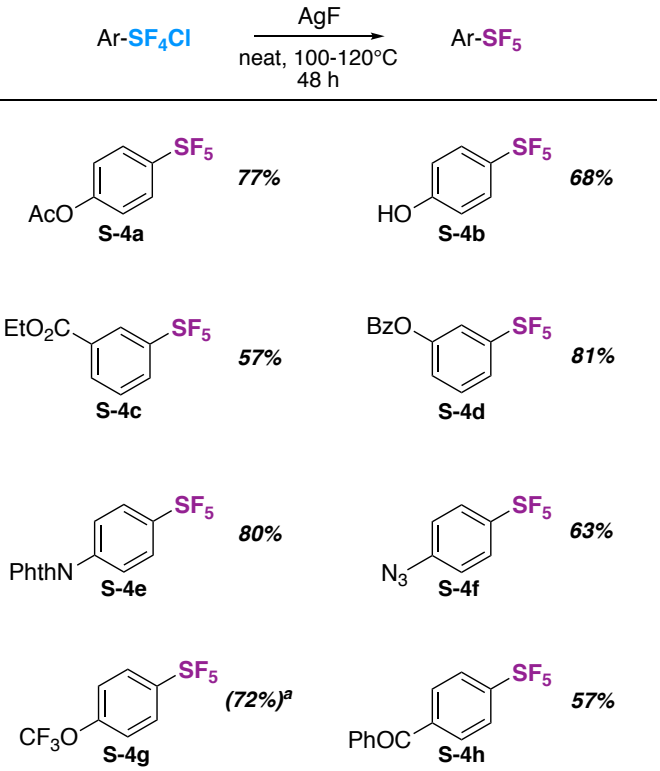
The obtained *trans*-isomer exhibits a distorted octahedral geometry around the sulfur atom with S–F bond lengths of 1.582(4) Å, 1.596(4) Å, 1.600(4) Å and 1.614(3) Å, and S–Cl and S–C bond lengths of 2.093(2) Å and 1.800(4) Å, respectively. The bond angles around the sulfur atom deviate only slightly from the perfect octahedral angles (i.e. C–S–F, 87.1(1)°; F–S–F, 88.9(2)°, 89.4(2)°, 90.4(2)° and 90.8(2)°; C–S–Cl, 178.3(2)°). Unfortunately, we were not able to crystallize a *cis* isomer of any of the described aryl-SF_4Cl species.

As this crystal structure was the first of its kind, no meaningful comparisons can be drawn at this point and the structure will be further discussed along with, and compared to that of aryl-SF_5 species below.

2.2.6 Synthesis and Characterization of Pentafluoro(aryl)-λ⁶-sulfanes

Having established the ability of the new TCICA/KF approach to facilitate access to a library of known and novel aryl-SF_4Cl compounds, it remained to be seen whether the generated intermediates are, indeed, viable precursors in the syntheses of aryl-SF_5 products. As discussed before, there are various established methods to afford the necessary Cl–F exchange reaction to choose from. The choice, in this case, fell on a straightforward method previously reported by Kanishchev et al. who used neat AgF together with the aryl-SF_4Cl derivatives at 120 °C to generate the aryl-SF_5 species.[96] Application of the unoptimized method to entries **S-2i**, **S-2m**, **S-2o**, **S-2q**, **S-2r**, **S-2w** and **S-2x** afforded their respective pentafluorosulfanyl derivatives in good yields (Table 6). Compound **S-4b** was easily obtained by a basic workup (LiOH) following the Cl–F exchange reaction otherwise leading to **S-4a**. It was also possible to obtain crystals suitable for XRD measurements for compounds **S-4e** and **S-4h** by slow evaporation of a solution of the former in $CDCl_3$ and by sublimation of the latter. Both are discussed in more detail below. Unfortunately, compounds **S-2y**, **S-2z** and **S-2aa** did not give their corresponding SF_5 derivatives upon treatment with AgF and the reactions resulted mainly in the formation of aryl-SO_2F instead. A different method to allow the Cl–F exchange for these heteroaromatic compounds has yet to be found.

Table 6: Scope of aryl-SF_5 species synthesized from aryl-SF_4Cl counterparts this thesis.



Isolated yields. ^{19}F NMR yields in brackets. [a]Pure isolated product was not obtained.

2.2.7 NMR Spectroscopic Details of Aryl-SF_5

In contrast to the above-mentioned aryl-SF_4Cl species, aryl-SF_5 compounds cannot exhibit isomerism. Their ^{19}F NMR spectra are nevertheless interesting and shall be discussed briefly. All aryl-SF_5 (and alkyl for that matter) species show a very characteristic ^{19}F NMR pattern due to their unique structure. Whereas the axial fluorine will couple to the four equatorial F-atoms, resulting in a pentet pattern, the equatorial fluorine atoms are equivalent and thus couple only to the remaining, axial F-atom and, accordingly, appear as a doublet in the spectrum. To avoid a rather lengthy discussion of all compounds, the chemical shifts for both sets of signals were collected (MeCN-d_3, room temperature) averaged and reveal the following mean values: 84.02 ± 0.96 ppm and 63.34 ± 0.54 ppm for the axial and equatorial F-atom, respectively. Furthermore, the spectrum of **S-4f** is shown in Figure 13 as an example.

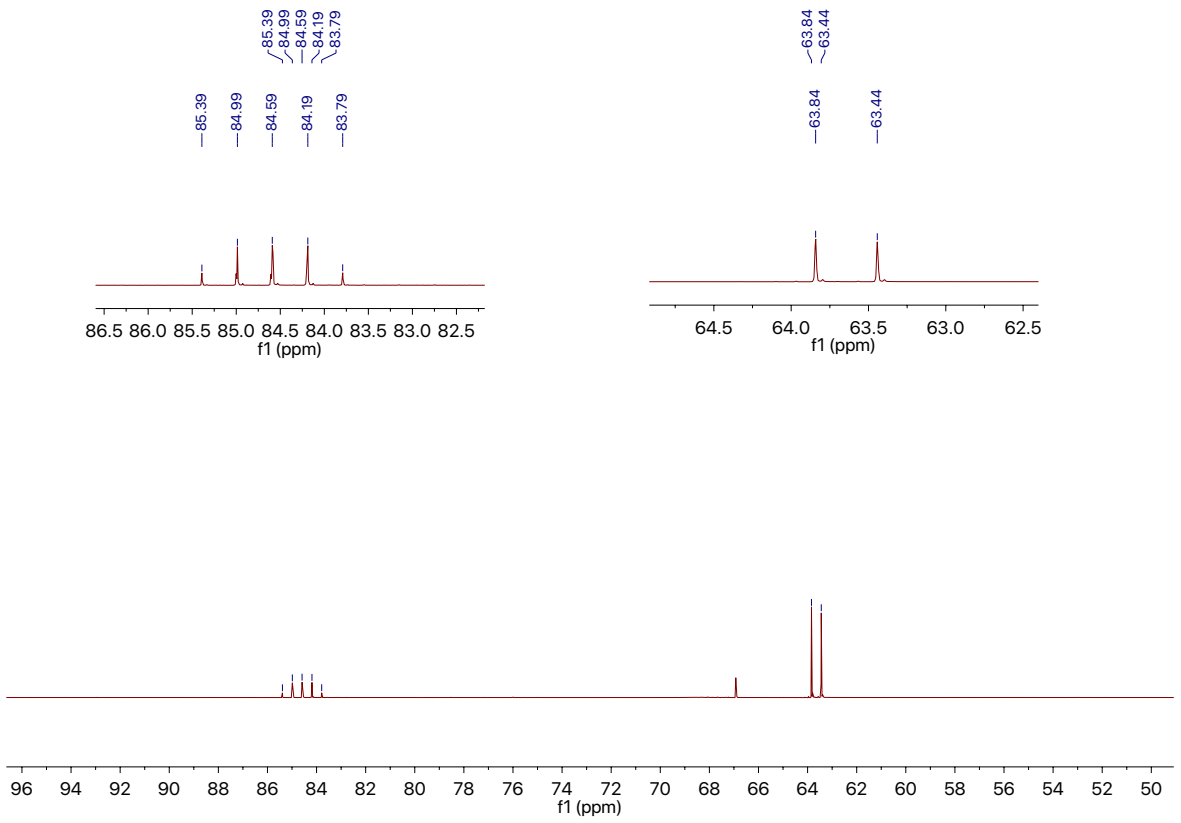


Figure 13: ^{19}F NMR spectrum of **S-4f**. Labelled signals belong to the *cis*-SF_5 group.

2.2.8 Solid State Analysis of a Representative Aryl-SF_5 Derivative

As mentioned above, apart from the obtained crystal structure for SF_4Cl derivative **S-2ab**, we were also able to collect XRD data for crystals of compounds **S-4e** and **S-4h** (Figure 14). Especially compound **S-4e** became important later, when compared to an analogous tellurium species and is thus discussed at length with the latter in chapter 3. However, a short discussion over the general geometry, bond lengths and angles of **S-4h** is given to provide an overview of the bonding properties in such molecules. The compound was previously prepared using a building block approach from 4-aminophenylsulfurpentafluoride and subsequently crystallized by Yamashita and coworkers in 2012.[103] The bond lengths around the sulfur atom take the values of 1.583(4) Å for the S–F_{ax}, 1.574(3) Å, 1.581(4) Å, 1.586(3) Å and 1.590(4) Å for the S–F_{eq} and 1.793(6) Å for the S–C bond. Note, there is no significant (threefold standard deviation) difference in S–F bond lengths when comparing axial and equatorial bonds, a dissimilarity as compared to pentafluoro tellanes, to be discussed later in chapter 3. The molecule exhibits a slightly distorted octahedral geometry around the sulfur central atom with a C–S–F_{ax}, bond angle of 179.5(2)°, a C–S–F_{eq}, bond angles of 92.1(2)°, 92.3(2)°, 92.7(2)° and 92.8(2)° and F_{eq}–S–F_{eq} angles of 89.7(2)° and 89.9(2)°. The equatorial fluorine atoms are thus bent away from the arene and towards the axial F-atom. Comparison to **S-2ab** reveals no significant elongation of the S–C bond (S–C = 1.800(4) Å in **S-2ab**) and only a minor elongation of the S–F_{eq} bonds ($\bar{d}$(S–F_{eq}) = 1.598 Å) in **S-2ab**.

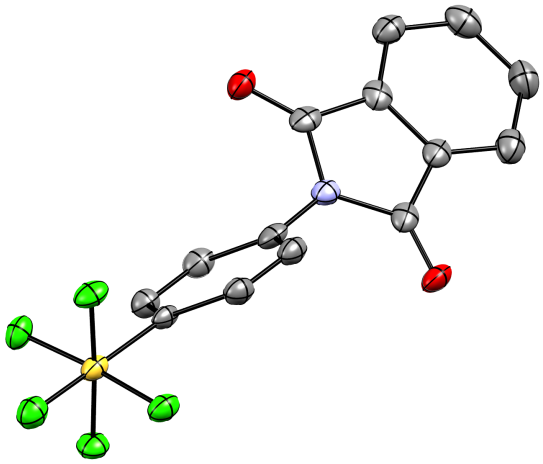


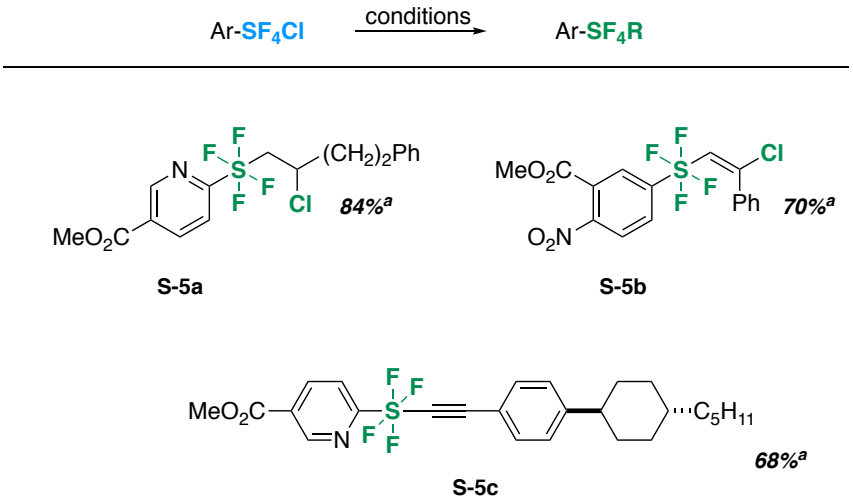
Figure 14: ORTEP view of **S-4h** (displacement ellipsoids at 50% probability level). Hydrogen atoms omitted for clarity.

2.2.9 Beyond SF_5 Chemistry – Tetrafluoro(aryl)(organyl)sulfane Chemistry and Investigations with Diselenides

Introductory Remark: Other than the detailed analysis of aryl-SF_4Cl and aryl-SF_5 compounds, we used the TCICA/KF chemistry to explore two further topics: 1) SF_4Cl reactivity that deviates from the regular use as an intermediate to SF_5 bearing molecules and 2) application of the TCICA/KF approach to other dichalcogenides.

Firstly, a short discussion of the former subject is provided in the following paragraph. Having successfully investigated its applications in SF_5 chemistry, we turned to uses of the SF_4Cl group previously described by the Welch[99] and Shibata[104] groups. Both have shown that aryl-SF_4Cl intermediates can be used to make more unusual aryl-SF_4R (R = alkyl, alkenyl, alkynyl) compounds that are, similar to aryl-SF_5 species, chemically relatively inert and allow for subsequent modification if they bear strong electron-withdrawing substituents. With that knowledge in mind, we proceeded to show that some aryl- and heteroaryl-SF_4Cl compounds in Table 3 can be converted into isolable aryl-SF_4-containing derivatives (Table 7). Thus, we were successful in the synthesis of compounds bearing alkyl (**S-5a**) and alkenyl (**S-5b**) groups by treatment of **S-2p** and **S-2n** respectively with catalytic triethyl borane in DCM at room temperature for 1 h, followed by the addition of 4-phenyl-1-butene or phenylacetylene. Compound **S-5c**, which is reminiscent of liquid crystalline material, was obtained in a two-step procedure by analogous treatment of **S-2p** with catalytic triethyl borane in DCM at room temperature for 1 h, and subsequent addition of 1-ethynyl-4-((1s,4r)-4-pentylcyclohexyl)benzene followed by a basic elimination reaction with LiOH in DMSO for 48 h. All three compounds could be isolated in excellent yields by column chromatography. Slow evaporation of a saturated solution of **S-5a** in *n*-hexane:benzene (1:1) afforded crystals suitable for X-ray diffraction and so XRD data for **S-5a** could be collected and the structure is depicted in the appendix.

Table 7: Scope of aryl-SF_4R species synthesized from aryl-SF_4Cl counterparts this thesis.



Isolated yields. [a]Condition for synthesis described in text.

Besides the oxidative fluorination of disulfides, we were also interested in diselenides and ditellurides. The latter in particular were very productive in their reactivity with TCICA/KF and therefore provided the occasion for writing the separate chapter 3 (*vide infra*). The former, however, were not investigated in detail, so that the collected data will be summarized here.

The only diaryl diselenide tested with the TCICA/KF method to date is diphenyl diselenide (Ph_2S_2, **Se-1a**). The compound was treated with TCICA/KF keeping the same reaction conditions as for disulfides (18 equiv. TCICA, 32 equiv. KF). Surprisingly the reaction did not yield any $PhSeF_4Cl$ (or $PhSeF_5$ analogous to $PhTeF_5$) but was instead fully converted into $PhSeF_3$ (**Se-2a**, ^{19}F NMR yield = 95%). Even prolonged heating (90°C, 48 h), the addition of acids (KHF_2, TFA) or a solvent change (DCM, $MeNO_2$) did not yield any Se(VI) product. Due to time constraints, a project for the further development of aryl-SeF_3 or aryl-SeF_5 chemistry could not be completed. Interestingly, however, aryl-SeF_3 compounds are reported to act as difluorinating reagents, but studies on this topic have not resurfaced in the literature since 1998.[105] Since the only known synthesis of aryl-SeF_3 compounds requires stoichiometric and prohibitively expensive XeF_2 the reoccurring issue as for why this chemistry has been forgotten for over 20 years is again likely *synthetic accessibility*. Future main group and fluorine chemists are thus encouraged to explore the field of organoselenium fluorine chemistry for it might be worthwhile (even if only out of sheer curiosity).

2.3 Conclusion

A well-stocked library of tetrafluoro-λ^6-sulfanyl chlorides (aryl-SF_4Cl compounds) has been prepared using a new, mild and gas-reagent-free method that circumvents the reliance on hazardous fluorinating reagents and/or gas reagents (e.g. Cl_2) by employing easy-to-handle TCICA, KF and catalytic amounts of TFA. These simple conditions allow direct access to aryl-SF_4Cl intermediates, of which several are inaccessible using previously established methods. The compounds were characterized by NMR spectroscopy and a first crystal structure of an aryl-SF_4Cl compound is reported and briefly discussed. The newly obtained compounds have subsequently been evaluated for their ability to function as viable precursors in the synthesis of aryl-SF_5 species, by application of a standard Cl–F exchange reaction using AgF. Thereby a variety of novel aryl-SF_5 compounds were successfully synthesized and fully characterized by NMR and IR spectroscopy as well as mass spectrometry and, in two cases, X-ray diffraction measurements. Furthermore, the facile access to aryl-SF_4Cl species enabled an investigation into aryl-SF_4R chemistry by treatment of the former with triethyl borane followed by the addition of nucleophiles. Thereby, three new ester-functionalized aryl-SF_4R species were synthesized and characterized. Finally, the same TCICA/KF approach provided convenient access to aryl-SF_3 and aryl-SeF_3 compounds, extending the applications of this chemistry beyond aryl-SF_4Cl and aryl-SF_5-functionalization, and demonstrating its synthetic potential to address oxidative fluorination and its associated problems in general.

Chapter 3

Pentafluoro(aryl)-λ^6-tellanes: History, Synthesis, Structural Investigations and Reactivity

Parts of this chapter are published and have been adapted with permission from:

«Pentafluoro(aryl)-λ^6-tellanes and Tetrafluoro(aryl)(trifluoromethyl)-λ^6-tellanes: From SF_5 to the TeF_5 and TeF_4CF_3 Groups» **D. Bornemann**, C. R. Pitts, C. J. Ziegler, E. Pietrasiak, N. Trapp, S. Küng, N. Santschi, A. Togni, *Angew. Chem. Int. Ed.* **2019**, *58*, 12604–12608; *Angew. Chem.* **2019**, *131*, 12734–12738. DOI: 10.1002/anie.201907359

3.1 Introduction

3.1.1 Introductory Remark

A major part of this thesis focusses on tellurium and its fluorine compounds. The following subchapter shall serve as a quick overview of the chemistry of this element.

3.1.2 Tellurium – An Overview

The spot of the heaviest non-radioactive entry in the chalcogen group is taken by the semi-metal tellurium. Though on equal terms with gold when compared in their natural abundance, interest in the grey tellurium and tellurium chemistry pales in contrast to the treasured, shiny transition metal. This, however, hardly has negative consequences for the tellurium chemist as its price and the many yet unmade discoveries make tellurium an excellent candidate for fundamental research.

First discovered in 1782 by the Austrian chemist F. J. Müller von Reichenstein in gold ore, "aurum paradoxum" was only identified as a new metal by the German chemist M. H. Klaproth in 1797. As per custom, Klaproth was given the right to name the chalcogen and decided "[…] *borrowing the name of mother earth* […]" to name it tellurium (lat.: *tellus* "earth").[106]

Unlike its lighter homologues that exist in a variety of modifications (yellow Sulfur, red and yellow Selenium) only one form of elemental tellurium is known under standard conditions, namely the grey-black metallic Te^0.[18] In terms of reactivity, tellurium is very similar to both of its lighter congeners sulfur and selenium. When bound to other more electropositive elements, tellurium will appear in the oxidation state -II and will, when reacted with more electronegative compounds, appear in the oxidation states +II (e.g. $TeBr_2$), +IV (e.g. H_2TeO_3) or +VI (e.g. TeO_3 or TeF_6). Noteworthy, the oxidation state +VI is easier to access for sulfur and tellurium than for selenium (or polonium), which will become important later in the following chapter.[18]

Industrial applications of tellurium are still relatively rare and mainly focus on inorganic chemistry for alloying, the production of phase-change memory chips and semiconductors.[5] Organic chemistry knows a variety of organotellurium species with Te-C single bonds covering all accessible oxidation states from Te(-II) to Te(+VI).[107] Examples include tellurols (RTeH compounds), diorgano ditellurides (R_2Te_2 compounds), tetraorgano tellurides (R_4Te compounds) and more.[108] The first known organotellurium compound synthesized by Wöhler in 1840 was diethyl telluride.[109] So far, only a handful of organotellurium species are of synthetic interest for the chemical community as very few useful applications have been found to date. One of the more common uses focusses on Te compounds as reducing agents for organic substrates.[108] Key examples are the

reduction of carbonyl compounds to their corresponding alcohols with inorganic (Na_2Te, Al_2Te_3 , $TeCl_4$, etc.)[110–112] or organic (*i*-Bu_2Te, PhTeH, etc.)[110,112,113] tellurium compounds. Furthermore, imines,[111] enamines,[111,114] nitro derivatives,[110] arylalkenes[113–115] and alkynes[113–115] have been shown to be reduced by different Te compounds. It has to be stated, though, that to date tellurium has no large-scale academic or industrial application in organic synthesis. The reasons for the scant attention paid to the semi-metal are likely two-fold: i) tellurium is relatively rare (ca. 1 ppb abundance in the Earths continental crust) and ii) fundamental science with tellurium has still a vast ground for discoveries potentially leading to useful transformations making Te compounds interesting for research groups in academia and industry beyond just general curiosity.[5,107]

To put the topic of tellurium fluorine chemistry into perspective, the next subchapter will focus on the history of inorganic tellurium fluorides and derivatives thereof.

3.1.3 The Birth of Organometallic Tellurium Fluorine Chemistry

At first, the combination of the rare semi-metal tellurium with fluorine might strike the reader as rather exotic. It is thus even more astonishing that fluorine chemistry with this chalcogen was conducted already less than a century after its discovery in 1891. French Nobel laureate Henri Moissan, predominantly known for the isolation of elemental fluorine, was the first chemist reacting elemental tellurium with fluorine gas in a "violent reaction with inflammation" thereby obtaining the first manmade tellurium fluoride, tellurium hexafluoride.[116] It was, however, not until several years later in 1906 when Prideaux and co-workers systematically synthesized and analyzed the hexafluoride.[116] TeF_6 is a colorless highly toxic gas with a remarkably unpleasant smell, typical for volatile tellurium compounds. Nowadays it is usually synthesized by fluorination of TeO_3 with F_2.[18] Having a nearly perfect octahedral geometry around the central atom, tellurium hexafluoride exhibits a very similar coordination geometry as SF_6 or SeF_6, chemically, however, it is hardly comparable to its lighter, comparatively unreactive congeners.[18] The fluoride ligands in TeF_6 are easily replaced and so the compound undergoes stepwise hydrolysis to telluric acid ($Te(OH)_6$) upon contact with moisture.[116] The only two other homoleptic tellurium fluorides include TeF_4 and, presumably, Te_2F_{10}. The former is typically synthesized from TeO_2 and SF_4.[117] It is an extremely toxic, water-sensitive compound that adopts a see-saw like structure, in analogy to SF_4. The rather high dipole moment of TeF_4 renders the compound solid at room temperature. It is infrequently used as a fluorination reagent. On the other hand, ditellurium decafluoride is a controversially discussed, theoretically predicted compound, in close analogy to S_2F_{10}. Different research

groups had claimed to have made this compound in the 1950s and 1960s, but no indisputable evidence had been presented as for its existence.[118–120]

Reported ^{19}F NMR spectra, as well as other physical properties like melting point and refraction index, strongly resembled those of the known oxo-bridged TeF_5OTeF_5.[121,122] The elusive compound caused P. E. Watkins to write an article titled *Ditellurium Decafluoride – A Continuing Myth* about the compound, identifying mistakes made in both synthesis and analysis by different advocates of the molecule.[123] To date, no solid-state structure or clear $^{19}F/^{125}Te$ NMR evidence for the existence of Te_2F_{10} could be obtained and so the molecule remains part of the realm of theory for now.

Other than homoleptic fluorides, also mixed tellurium halides exist with the most noteworthy of them being TeF_5Cl. Synthesis of this compound is achieved by treatment of TeF_4 with ClF. Again, parallels can be drawn to the sulfur analogue SF_5Cl. Just like its lighter homologous compound, the tellurium derivative is a highly toxic gas and readily reacts, under the liberation of gaseous HCl and/or HF, with moisture and nucleophiles as discussed below.[18] Together with TeF_6, TeF_5Cl inspired tellurium-based coordination chemistry and led to a variety of TeF-derivatives mostly accessed by treatment of either compound with a nucleophile (HNu) to afford an array of $Te(Nu)_nF_{n-6}$ species with alcohols, amines and more.[124] These synthetic materials served as the foundation of what should later become organometallic tellurium fluorine chemistry. In spite of these early advances, the group of hexavalent Te(VI) fluorides remained significantly underdeveloped when compared to its lighter homologues, sulfur and selenium. All known derivatives of tellurium hexafluoride were structurally very similar, which is not surprising as the field knew only little more than a dozen compounds. But the groundwork for synthetic Te(VI) fluorine chemistry had been laid.

It was not, however, until Passmore had successfully synthesized $(CF_3CF_2)_2TeF_4$ in 1974 that the first "truly organometallic" Te(VI) fluoride with an intact Te–C bond had been discovered.[125] What followed was the synthesis of *cis*-bis(pentafluorophenyl)tetrafluoro tellane, by German chemists Klein and Naumann in 1985, marking the first observation of an aryl-Te(VI) fluoride.[126] The group discovered that the extremely electron-poor compound could only be obtained by fluorination of $(C_6F_5)_2Te$ with F_2 gas directly and even then, only after several hours. XeF_2 or other fluorination reagents were not strong enough oxidants to obtain the Te(VI) species

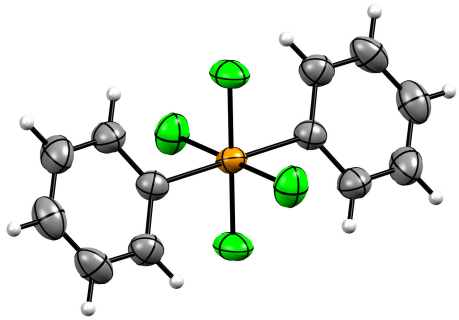
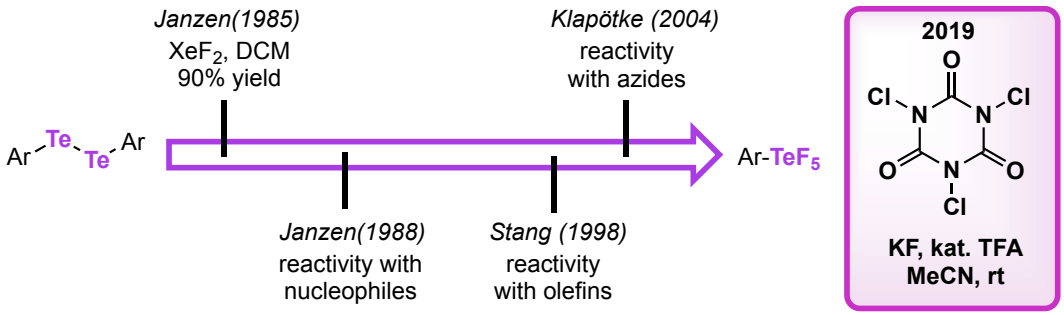


Figure 15: ORTEP view of *trans*-Ph_2TeF_4 as described by Klapötke *et al.* (displacement ellipsoids at 50% probability level).

and typically yielded the difluorinated Te(IV) species, R_2TeF_2, instead. The compound was, however, unstable and prone to hydrolysis and reaction with solvents at room temperature, making XRD analyses at the time impossible (It was only much later, in 2004, that Klapötke *et al.* obtained XRD data for diphenyltetrafluoro tellane which is depicted in Figure 15). The fact that the group still managed to characterize the compound by several spectroscopic methods (^{19}F NMR-, Raman- and IR-spectroscopy) as well as mass spectrometry is, frankly, remarkable. Further noteworthy contributions to the field were, firstly, the oxidative addition of TeF_5Cl to 1,1-difluoroethene by the Seppelt group in 1987 complementing the known reactivity of the related SF_5Cl and SeF_5Cl, secondly, spectroscopic and XRD analyses of *mer*-Ph_3TeF_3 carried out in the group of Janzen in 1985, describing the first crystal structure of any organotellurium(VI) compounds followed by the stereoselective access to *cis*- and *trans*-Ph_2TeX_4 (X = F, Cl) and the report of an X-ray structure (Figure 15).[127–129] Finally, the synthesis of $PhTeF_5$ by Janzen *et al.* and first reactivity studies thereof by Janzen, Stang and Klapötke unveiled the chemistry of this compound. However, the solid-state structure of the low-melting material remained unknown.[105,128,130,131] The compound class of aryl-TeF_5 species is of special interest for this thesis and will be discussed in detail in the following subchapters.

3.1.4 Pentafluoro(aryl)-λ⁶-tellanes – Remarks and Timeline

Research concerning pentafluoro(aryl)-λ⁶-tellanes (aryl-TeF_5 compounds) has been relatively scant even when compared to general tellurium chemistry. There have been only a handful of breakthroughs in the field and thus progress has been slow. The most important developments mentioned above are summarized in a timeline depicted in Scheme 2, which is supposed to function as a reference point for the reader when navigating though the following (sub)chapters.

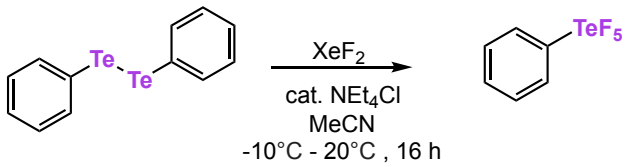


Scheme 2: Timeline with the most important developments in aryl-TeF_5 chemistry.

3.1.5 Pentafluoro(aryl)-λ⁶-tellanes – First Steps

After Passmore had reported the synthesis of the first perfluoroalkyltellurium(VI) halide from TeF_5Cl and thus founded the field of organofluorotellurium chemistry, Janzen and coworkers managed to produce the first aryl-TeF_5 species in 1985 (Scheme 3).[125,128]

The researchers explored the reactivity of various organotellurides, namely diphenyl ditelluride, diphenyl telluride, triphenyl fluorotelluride, triphenylchloro telluride and tetraphenyl telluride, with XeF_2 and were consequently able to isolate and analyze the fluorinated derivatives $PhTeF_5$, Ph_2TeF_4, Ph_3TeF_3, Ph_3TeF_2Cl and Ph_4TeF_2, respectively.



Scheme 3: First described synthesis of $PhTeF_5$ from diphenyl ditelluride and XeF_2 by Janzen *et al.*

The compounds were characterized by ^{19}F and ^{125}Te NMR spectroscopy, mass spectrometry as well as elemental analysis. Unfortunately, no XRD data was collected. Shortly after their initial discovery, Janzen and coworkers improved the synthesis of $PhTeF_5$ by addition of catalytic NEt_4Cl to Ph_2Te_2 and XeF_2.[94] Moreover, they investigated the hydrolytic stability of $PhTeF_5$ and *cis*- or *trans*-Ph_2TeF_4 in a follow-up publication.[129] Analogous to TeF_6, $PhTeF_5$ decomposed to the respective $PhTe(OH)_5$ over time. Noteworthy, the stepwise reaction proceeds increasingly slow, with the first substitution of a fluoride for a hydroxo ligand happening within seconds and all following substitutions taking minutes to hours. ^{19}F NMR analysis was used to confirm that substitution begins with one of the fluorides in *cis*-position to the phenyl ring. This reactivity will be discussed in more detail below. Interestingly, the decomposition of *trans*-Ph_2TeF_4 is significantly slower, showing more than 90% intact product after seven days in aqueous solution at 60 °C. The authors attributed the stability to the relative bulkiness of *trans*-Ph_2TeF_4 in comparison to its monoarylated counterpart. Furthermore, replacement of one fluoride ligand for another phenyl-ring results in significantly lowered Lewis acidity, making the compound more resistant towards nucleophilic attacks.

Inspired by the hydrolytic instability of the organofluoro tellurides, Janzen and coworkers contributed another paper discussing the reactivity of $PhTeF_5$, *trans*-Ph_2TeF_4 and *mer*-Ph_3TeF_3, with an array of nucleophiles in 1988/89.[130] All compounds were reacted with dimethyl- and diethylamine, methanol and their trimethylsilyl derivatives. The results of their findings are summarized in Table 8.

Table 8: First reactivity study of organofluoro tellurides with nucleophiles by Janzen *et al.*

Starting material	Nucleophile	Product
$PhTeF_5$	MeOH	*cis*-$PhTeF_4OMe$
$PhTeF_5$	$TMSNMe_2$	*cis*-$PhTeF_4NMe_2$
trans-Ph_2TeF_4	MeOH	Ph_2TeF_3OMe
trans-Ph_2TeF_4	$TMSNMe_2$ or $HNMe_2$	$Ph_2TeF_3NMe_2$
trans-Ph_2TeF_4	$TMSNEt_2$	$Ph_2TeF_3NEt_2$
Ph_3TeF_3	MeOH	Ph_3TeF_2OMe
Ph_3TeF_3	$HNMe_2$	$Ph_3TeF_2NMe_2$

In good agreement with their finding for the hydrolysis of $PhTeF_5$, the resulting products showed exclusively *cis*-substitution and only one fluoride ligand was replaced in all cases. The latter part remains true for *trans*-Ph_2TeF_4 and *mer*-Ph_3TeF_3. In a side note, the authors also reported the formation of the minor side product *cis*-Ph_2TeF_4 in the reaction of Ph_2Te_2 with XeF_2.

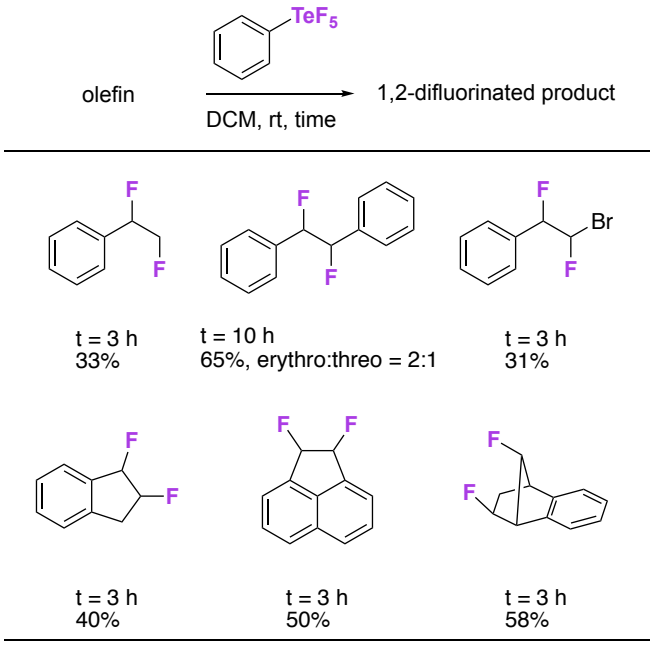
After Janzen *et al.* investigated the synthesis and reactivity of aryl-TeF_5 species, silence fell around the field of organofluoro tellurium chemistry. It was not until ten years later in 1998 when Stang *et al.* picked up the topic again and investigated the potential of $PhTeF_5$ as a fluorination reagent.[105] In their publication, the group described the use of $PhSeF_3$, $PhSeF_5$ as well as $PhTeF_5$ as effective fluorination reagents for a large collection of olefins. Preparation of the latter was achieved following the initial synthetic procedure reported by Janzen that generated $PhTeF_5$ from Ph_2Te_2 and XeF_2 without additives (i.e. without NEt_4Cl).[128] Noteworthy, Stang *et al.* described the full conversion of the starting material within 5 – 10 min, contrasting the reported 4 hours by Janzen.[94,128] Furthermore, the group mentioned that the resulting products were used without purification in the subsequent fluorination attempts even though, under the used conditions, formation of $PhTeF_5$ was incomplete and only ever observed in modest yields at best. Thus, significant contamination with XeF_2 of the crude product could be expected. By close analysis of the literature two diametrically opposed statements about the synthesis of $PhTeF_5$ quickly catch the eye. An abbreviated version of those statements is given here:

Janzen, **2000**[94]: *"[…] As reported previously (authors note: in their 1985 publication), the formation of $PhTeF_5$ (authors note: from Ph_2Te_2 and XeF_2) occurs slowly over a period of 4 h in modest yield in the absence of Et_4NCl. […]"*

Stang, **1998**[105]: *"[…] The conversion of Ph_2Se_2 needs 3–4 h but Ph_2Te_2 reacts faster (5–10 min) (authors note: to $PhTeF_5$). The reactions were monitored by Xe evolution (gas burette, usually 95–100 vol.% of Xe evolved). Both reagents were used without isolation. […]"*

These obviously contradicting statements, and especially the final sentence of the latter citation will be further addressed below. However, following the paper by Stang *et al.* it is apparent that treatment of olefins with $PhTeF_5$ resulted in the formation of their 1,2-difluorinated derivatives as shown in Table 9.

Table 9: Scope for the oxidative difluorination of olefins reported by Stang *et al.*



Note, all experiments conducted in this study were exclusively monitored by ^{19}F NMR spectroscopy and side products or the resulting tellurium species were never closely analyzed. Hence, it was not possible to discuss the mechanism by which the difluorination supposedly occurs or what side products are formed, though the authors hinted at $PhTeF_3$ formation as a likely option.

It took again another six years before the next group, this time Klapötke *et al.*, took up the challenge of $PhTeF_5$ chemistry in 2004.[131] The group focused on derivatization reactions starting from different organofluoro tellurides with $TMSN_3$ as shown in Table 9. Concerning the synthesis of $PhTeF_5$ the group relied on the findings of the 80ies by Janzen, treating Ph_2Te_2 with XeF_2 and catalytic NEt_4Cl. In agreement with the Janzen group, Klapötke *et al.* also described a fast oxidative fluorination of Ph_2Te_2 to $PhTeF_3$ followed by a slow second oxidation step to $PhTeF_5$, and thus mentioned the requirement for NEt_4Cl as a catalyst. The derivatization reactions were carried out at room temperature in DCM with varying amounts of TMS reagent.

Table 10: Summary of the reactivity study of organofluoro Te(VI) compounds with $TMSN_3$ as reported by Klapötke *et al.*[131]

Starting material	Reactant	Product
$PhTeF_5$	5 equiv. $TMSN_3$	$Ph_2Te(N_3)_2 + TeF_4 + N_2$
trans-Me_2TeF_4	4 equiv. $TMSN_3$	$Me_2Te(N_3)_2 + TeF_4 + N_2$
trans-Ph_2TeF_4	4 equiv. $TMSN_3$	$Ph_2Te(N_3)_2 + TeF_4 + N_2$
cis-Me_4TeF_2	2 equiv. $TMSN_3$	$Me_2Te(N_3)_2 + [Me_3Te]N_3 + N_2$
mer-Me_3TeF_3	3 equiv. $TMSN_3$	$Me_2Te(N_3)_2 + [Me_3Te]N_3 + N_2$
mer-Ph_3TeF_3	3 equiv. $TMSN_3$	$Ph_2Te(N_3)_2 + [Ph_3Te]N_3 + N_2$

As summarized in Table 10 organofluoro tellurides are susceptible to nucleophilic substitution (similar to TeF_6) leading, in all cases, to Te(IV) compounds of the general formula $R_2Te(N_3)_2$ (R = Me, Ph). Interestingly, the procedure always involves concomitant reduction of the used Te(VI) species under oxidation of the azide ligand to N_2 and thus, the corresponding Te(VI) azides could not be observed.

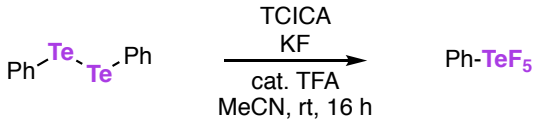
Subsequently, in the years following the publication by Klapötke, $PhTeF_5$ chemistry received little to no attention from the scientific community. An explanation for this negligence can, again, likely be found in one or both of the following observations. Firstly, potential applications of tellurium for the broader chemical audience have yet to be found and thus, interest in the element and its chemistry remains restricted within the domain of the few laboratories still carrying out fundamental main group chemistry. And secondly, synthetic access to $PhTeF_5$ is limited to laboratories having the know-how and equipment to work not only with toxic organotellurides but first and foremost with F_2 or XeF_2.
To be provided with both, the freedom to carry out fundamental tellurium chemistry, as well as the theoretical and practical knowhow necessary to conduct the required fluorination experiments, is a privilege that only very few chemists around the world share. In the case of this thesis, however, neither moral, intellectual nor financial support, were limited and thus the author was lucky enough to be allowed to conduct the experiments and gather the information about organofluoro tellurium chemistry summarized in the following sections.

3.2 Results and Discussion

3.2.1 Screening

After the great success we had with the application of the TCICA/KF approach to diaryl disulfides and diselenides (see chapter 2), it seemed natural to extend the procedure to ditellurides. Therefore, we carried out initial test experiments with Ph_2Te_2 (**Te-1a**), the only commercially available ditelluride, hoping to obtain $PhTeF_4Cl$ in the process. It came to our surprise that, in contrast to the sulfur chemistry, Ph_2Te_2 reacted with TCICA/KF to form its pentafluoro(phenyl)-analogue $PhTeF_5$ (**Te-2a**) directly and no second step in the form of a Cl–F exchange is required. Having obtained those encouraging first results we proceeded to screen for optimal conditions for the oxidative fluorination with TCICA and KF. We decided, like in the case of disulfides, to screen TCICA and KF equivalents, solvents and additives. The results of the screening are summarized in Table 11.

Table 11: Screening for optimized conditions of the oxidative fluorination of Ph_2Te_2.



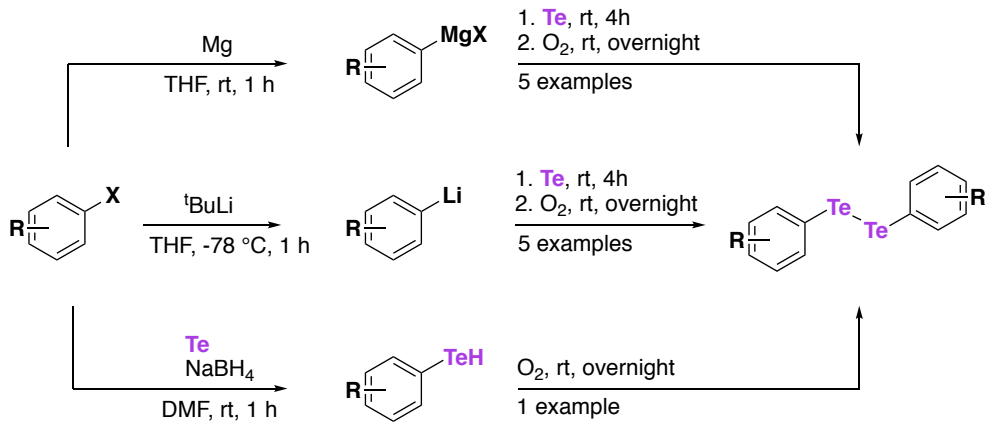
entry	*TCICA(equiv.)*	*KF (equiv.)*	*TFA (equiv.)*	*yield (%)*	*notes*
1	18	32	0.1	80	-
2	18	32	-	69	-
3	18	16	0.1	80	-
4	9.0	32	0.1	80	-
5	9.0	16	0.1	71	-
6	4.5	16	0.1	71	-
7	**6.0**	**24**	**0.1**	**86**	-
8	6.0	24	-	78	40 °C
9	6.0	24	0.2	73	-
10	6.0	24	0.5	28	-
11	6.0	24	0.1	78	2 x conc.
12	6.0	24	0.1	0	$MeNO_2$
13	6.0	24	0.1	0	EtOAc
14	6.0	24	0.1	0	acetone
15	6.0*	24	0.1	0	*NCS
16	6.0**	24	0.1	0	**NCPhth
17	6.0	24	0.1***	82	***$ZnCl_2$

The reactions were carried out in non-deuterated solvents and monitored by ^{19}F NMR spectroscopy, yields given here are thus ^{19}F NMR yields. Best yields of $PhTeF_5$ were obtained when 6 equiv. TCICA and 24 equiv. KF were used. As discussed for the disulfide substrates the yield of the reaction can be improved by addition of catalytic amounts of acid. We screened both Lewis and Brønsted acids and it did not seem to matter which type of acid was used in the process. The use of liquid TFA rather than $ZnCl_2$ or other metal salts is preferred simply for reasons of practicality. In analogy to disulfides, oxidation of Ph_2Te_2 to $PhTeF_5$ can only be observed when TCICA is applied as an oxidant. Both NCS or NCPhth are no suitable replacements for TCICA and did not yield any product formation, even with increased reaction times or after prolonged periods of heating (60 °C). Furthermore, in direct comparison to disulfide substrates, the amount of oxidant required is reduced in the tellurium case. This is likely a consequence of a lower reduction potential in tellurium compounds vs. sulfur analogues. When focusing on the solvent, best results were again obtained with MeCN. The use of $MeNO_2$, EtOAc, or acetone instead led to no visible product formation. Noteworthy, the reaction does not benefit from heating to 40 °C in terms of yield or reaction rate. Substitution of the fluoride source KF with CsF led to comparable yields.

In summary, it was determined that the highest ^{19}F NMR yields of 86% $PhTeF_5$ can be obtained by stirring Ph_2Te_2 with 6 equiv. TCICA, 24 equiv. KF and 10% TFA in MeCN overnight.

3.2.2 Synthesis of Diaryl Ditellurides

With optimized reaction conditions in hand, we wanted to explore the scope of the reaction next. Therefore, we proceeded with the preparation of a library of diaryl ditellurides (see appendix for a comprehensive list with numbered compounds). For the synthesis of all ditellurides except **Te-1j**, the procedures of Singh and Stefani[132] or Engman and Persson[133] were followed (Scheme 4).



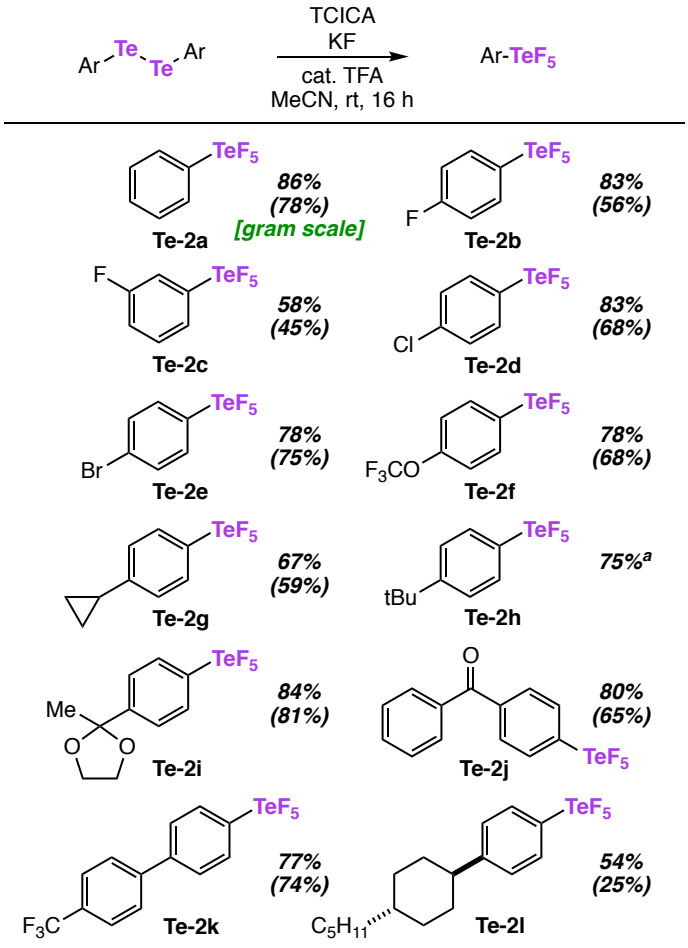
Scheme 4: Routes followed for the synthesis of diaryl ditellurides.

They described the reaction of elemental tellurium powder with nucleophilic aryl-Grignard or aryl-lithium reagents, respectively, leading to the formation of aryl-tellurolates (anionic aryl-Te species) which are oxidized in situ by reaction with atmospheric oxygen.
The literature procedures generally worked well and gave the resulting tellurides (**Te-1a** – **Te-1m**) in moderate to good yields (54–99 %).
In the case of R = 4-benzophenoyl (**Te-1j**) a method by Zhou was applied instead.[134] Therefore, NaHTe was produced in situ (by the reaction of Te with $NaBH_4$)[135] and reacted with 4-bromobenzophenone, followed by quenching with atmospheric oxygen. The ditelluride could thus be obtained in 54% yield.
Ditellurides with R = *para*-cyclopropyl or *para*-trifluoromethoxy were previously unknown and were thus fully characterized upon isolation.

3.2.3 Synthesis and Characterization of Pentafluoro(aryl)-λ⁶-tellanes

Application of the newly optimized reaction conditions for the oxidative fluorination of diaryl ditellurides allowed us to investigate both the scope of the reaction as well as its limitations (Table 12). The reaction tolerates standard electron-withdrawing groups well in the *meta*- and *para*-positions, such as halido (**Te-2b** – **Te-2e**) and a trifluoromethoxy substituent (**Te-2f**). An initial oxidative fluorination attempt using a substrate with an *ortho*-fluoro substitution pattern resulted in an unclear and complicated ^{19}F NMR spectrum; the TeF_5 group might be too large to form selectively in the presence of *ortho*-substituents, though the effect may not be purely a steric one. This was, however, not further investigated.

Table 12: Reaction scope of aryl-TeF_5 species synthesized in this thesis.



^{19}F NMR yields. Yields for compounds that could be isolated by extraction in brackets. [a]Pure isolated product was not obtained.

Additionally, mild electron-donating groups are tolerated in the form of cyclopropyl (**Te-2g**), *tert*-butyl (**Te-2h**), and acetal (**Te-2i**) substituents. Concerning the latter case, note that ketones do not necessarily require protection as acetals; for example, benzophenone derivative **Te-2j** was formed in good yield under TCICA/KF conditions. Purification of all compounds can be achieved without column chromatography, by extraction of the aryl-TeF_5 species into dry *n*-hexane, subsequent filtration and solvent evaporation.

As in the case of disulfide substrates, stronger electron-donating groups or alkyl groups with benzylic sites, can suffer from known background reactions with TCICA (e.g. ring or benzylic chlorination).[101] For instance, we found that an unsubstituted biphenyl ditelluride is electron-rich enough for unselective ring chlorination to be problematic, resulting in crystals that revealed the structure shown in Figure 16, **Te-2m**. Due to a difficult workup, no yield could be determined for **Te-2m**. Conversely, biphenyl ditellurides substituted with electron-withdrawing groups, for example, a CF_3 group, convert to their corresponding aryl-TeF_5 products selectively (**Te-2k**). In addition, we were able to access the slightly more complex compound **Te-2l**, albeit in lower yield, whose overall structure is reminiscent of a liquid crystalline material. Note, like in the aryl-SF_4Cl case, the reactions were typically carried out on a 100–200 mg scale but the reaction can easily be upscaled to 2 g, as shown for **Te-2a**.

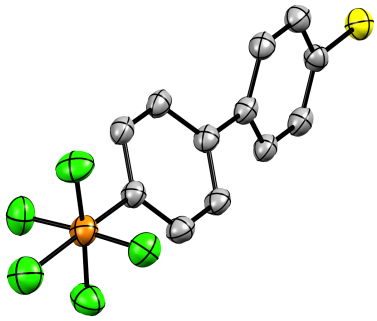


Figure 16: ORTEP view of **Te-2m** (displacement ellipsoids at 50% probability level). Hydrogen atoms are omitted for clarity.

3.2.4 NMR Spectroscopic Details of Aryl-TeF_5

Having obtained this series of aryl-TeF_5 compounds it was possible to conduct a first in-depth study of the spectroscopic properties of the TeF_5 group. Hence, the NMR spectra of all compounds were collected and analyzed. Most interesting are the corresponding ^{19}F NMR spectra. As an example, **Te-2a** shows two sets of signals in its ^{19}F NMR spectrum, a doublet at δ = -53.39 ppm corresponding to the four equatorial F atoms and a pentet at δ = -37.10 ppm for the axial F atom with a coupling constant of $^2J(F–F) \approx 151$ Hz (Figure 17). This general pattern is characteristic for aryl-TeF_5 species. The observed shoulders arise due to different natural abundances of the tellurium isotopes in the sample, mainly ^{130}Te (33.8%) ^{128}Te (31.7%) and ^{126}Te (19.0%). As ^{125}Te is an NMR active nucleus (natural abundance = 7.07%), its chemical shift was also measured and the very broad signal appears at 709 ppm with respect to Me_2Te.

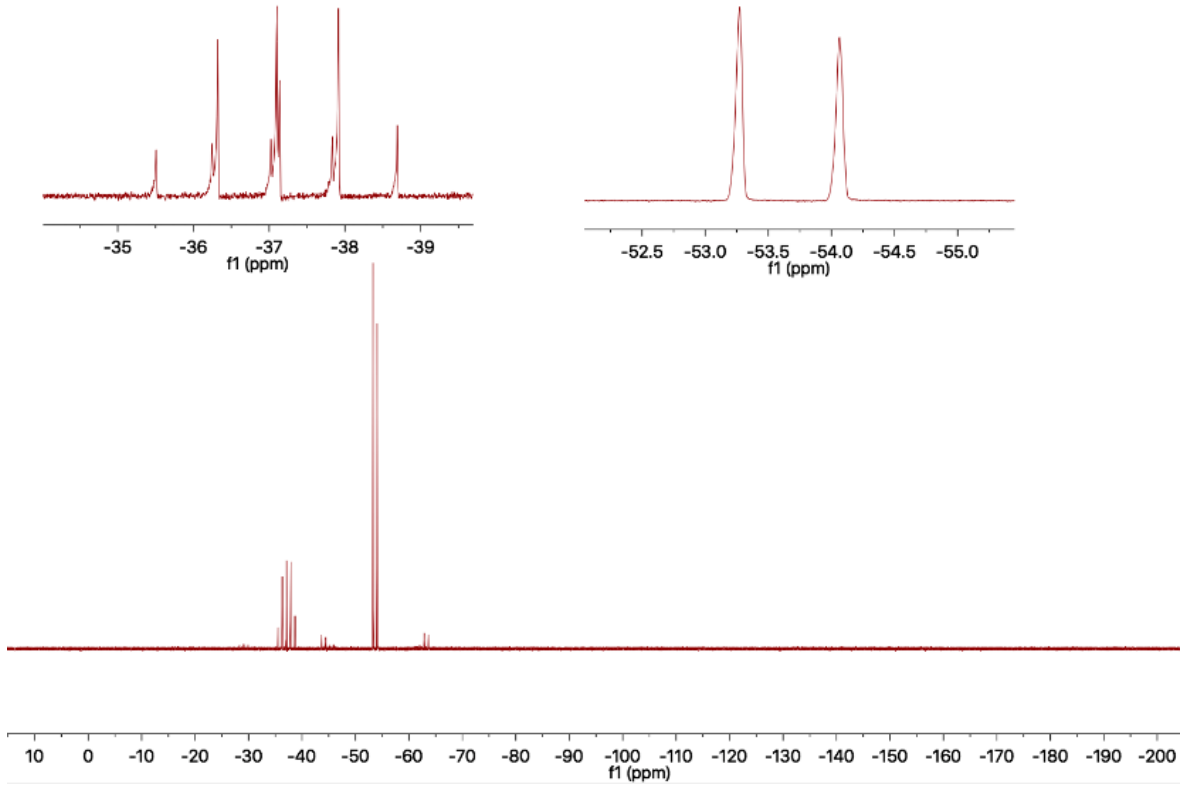


Figure 17: Exemplary ^{19}F NMR spectrum of **Te-2a**. Enlarged are the doublet and pentet characteristic for aryl-TeF_5 species.

Naturally, also ^{125}Te satellites can be observed with a ^{1}J(Te–Feq) coupling constant of 3602 Hz and ^{1}J(Te–Fax) of 3044 Hz which were determined from the ^{19}F NMR spectra.

An obvious comparison lies in the TeF_5 group versus the SF_5 group. In ^{19}F NMR experiments, drastic chemical shift differences in both the equatorial and axial fluorine atoms on phenyl-TeF_5 (ca. -53 and -37 ppm, respectively) are observed relative to phenyl-SF_5 (ca. + 63 and + 85 ppm), though ^{2}J(F–F) coupling constants are nearly identical at ca. 150 Hz. Additionally, in the IR spectra, the Te–F asymmetric stretching frequencies of **Te-2** derivatives at 655 cm^{-1} are significantly red-shifted from the corresponding S–F stretches of phenyl-SF_5 ($\tilde{\nu}$ = 831 cm^{-1}). This is in line with the expectedly weaker Te–F bonds, as also observed in the substitution reactions and crystal structure (*vide infra*).

3.2.5 Solid State Analysis of TeF_5

As 1) the aryl-TeF_5 compounds in Table 12 were unexpectedly stable in air and easy to isolate and 2) the solid-state structure of aryl-TeF_5 is heretofore unknown, we grew several single crystals that proved suitable for X-ray diffraction measurements. Typically, crystallization was achieved by slow evaporation of a saturated solution of the aryl-TeF_5 compounds in *n*-hexane.

Apart from compound **Te-2m** we were able to also obtain crystals for derivatives **Te-2d**, **-2e**, **-2g**, **-2i**, **-2j**, and **-2k**. To allow a more facile overview of the structural features of the aforementioned compounds, their most important bond lengths and angles are summarized in Table 13.

Table 13: Selected bond lengths and angles for compounds **Te-2d**, **-2e**, **-2g**, **-2i**, **-2j**, **-2k** and **-2m**. For multiple occurrences averaged values are printed in italics and the ranges are given in brackets.

	d(C-Te)/Å	d(Te-Fax)/Å	d(Te-Feq)/Å	C-Te-Fax/°	C-Te-Feq/°
Te-2d	2.057(4)	1.827(2)	1.853(1)	180	94.2(3)
Te-2e	2.063(8)	1.847(6)	1.856(3)	180	94.2(3)
Te-2g	2.072(2)	1.851(1)	*1.860* (1.855(1)-1.864(1))	179.4(2)	*95.2* (94.4(3)-95.8(2))
Te-2i	2.073(2)	1.836(2)	*1.857* (1.853(2)-1.862(2))	178.9(5)	*94.3* (93.7(5)-95.2(5))
Te-2j	2.077(2)	1.835(2)	*1.848* (1.837(2)-1.854(2))	179.0(5)	*94.4* (93.7(5)-95.5(5))
Te-2k	*2.044* (2.019(9)-2.061(15))	*1.841* (1.829(9)-1.852(6))	*1.828* (1.793(12)-1.858(12))	*177.8* (177.2(7)-178.4(8))	*94.1* (91.8(8)-96.9(8))
Te-2m	2.068(4)	1.832(2)	*1.861* (1.856(3)-1.863(2))	179.2(1)	*94* (93.4(1)-94.6(1))

Analysis of the XRD data shows that the TeF_5 group exhibits the expected slightly distorted octahedral geometry, as shown by the representative structure (compound **Te-2i**) in Figure 18. Examination of the bond lengths around the Te atom in these seven structures indicates average d(C_{ipso}–Te) = 2.065 Å, average d(Te–F_{ax}) = 1.838 Å, and average d(Te–F_{eq}) = 1.852 Å. Note that the average lengths of the Te–F_{eq} bonds are greater than the Te–F_{ax} bonds, indicating weaker equatorial Te–F interactions, which is in good agreement with the experimental findings in the literature showing an initial replacement of an equatorial F atom instead of an axial F atom in $PhTeF_5$. Additionally, the average θ(C–Te–F_{ax}) of 179.48° does not deviate significantly from linearity; however, an average θ(C–Te–F_{eq}) of 94.48° indicates that the four equatorial fluorine atoms point away from the arene.

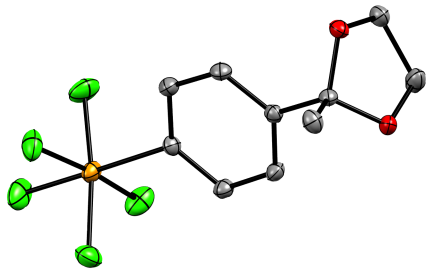
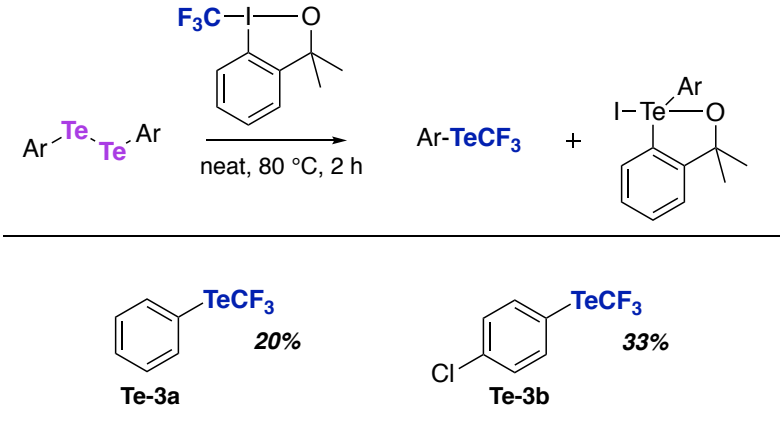


Figure 18: ORTEP view of **Te-2i** (displacement ellipsoids at 50% probability level). Hydrogen atoms are omitted for clarity.

3.2.6 Synthesis, Characterization and Structural Properties of Tetrafluoro(aryl)(trifluoromethyl)-λ⁶-tellanes

Beyond diaryl ditelluride substrates, we became interested in the oxidative fluorination of aryl-$TeCF_3$ compounds. Syntheses of aryl-$TeCF_3$ compounds have been developed by Umemoto and Ishihara,[75] and more recently by Schönebeck[136] and in our laboratory.[137] Based on recent work in the area, expertise in the trifluoromethylation of ditellurides was present in our group and a range of ditellurides had already been synthesized earlier in this work. We, therefore, opted for the procedure involving the trifluoromethylation of diaryl ditellurides by reaction with 1,3-dihydro-3,3-dimethyl-1-(trifluormethyl)-1,2-benziodoxol neat at 80 °C as shown in Scheme 5.



Scheme 5: Synthesis of aryl-$TeCF_3$ compounds as published in our group.

Because the reaction produces stoichiometric amounts of a Te(IV) compound as the second main product, the maximal theoretical yield of the desired compound is 50%. We applied the procedure to **Te-1a** as well as **Te-1d** and obtained compounds **Te-3a** and **Te-3b** as yellow liquids with an extremely unpleasant smell that were purified by distillation resulting in 20 and 33% yield respectively. As the starting material was not abundant we decided to omit screening and instead use the conditions we had already applied in the oxidative fluorination of diaryl ditellurides. To our satisfaction, under TCICA/KF conditions, we were able to convert phenyl-$TeCF_3$ to *trans*-phenyl-TeF_4CF_3 (**Te-4a**) obtaining the product in 80% isolated yield as a colorless oil (Figure 19).

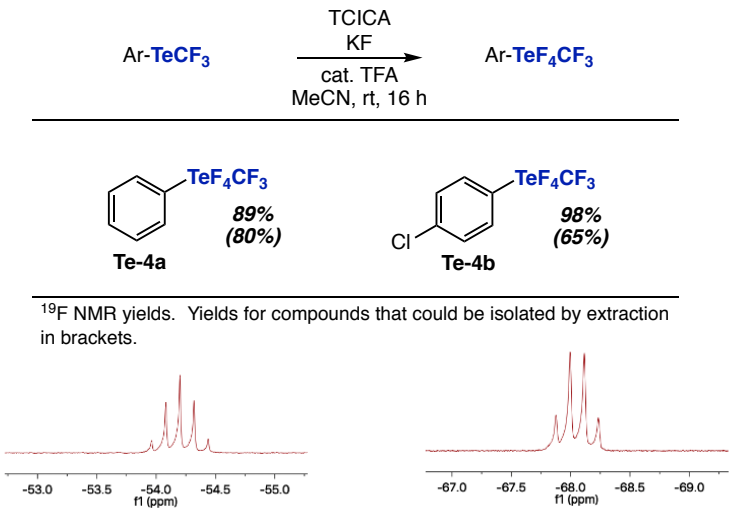


Figure 19: **Top**: Scope of the oxidative fluorination of $TeCF_3$ compounds **Te-3a** and **Te-3b**. **Bottom**: ^{19}F NMR spectrum of **Te-4a.** Enlarged are the pentet and quartet characteristic for the TeF_4CF_3 group.

As this is, to our knowledge, the first time this TeF_4CF_3 group has been observed, we also synthesized *para*-chloro derivative **Te-4b** as an off-white solid with the aim of obtaining X-ray diffraction data (discussed in more detail below). Regarding ^{19}F NMR spectra, **Te-4a** and **Te-4b** show the patterns expected for their highly fluorinated nature. Again, taking phenyl-derivative **Te-4a** as an example: Two sets of signals can be observed, slightly upfield shifted from the equivalent aryl-TeF_5 case, a quartet at δ = -68.80 ppm corresponding to the equatorial F atoms directly bound to Te and a pentet at δ = -54.20 ppm for the trifluoromethyl group, both exhibiting much weaker coupling constants

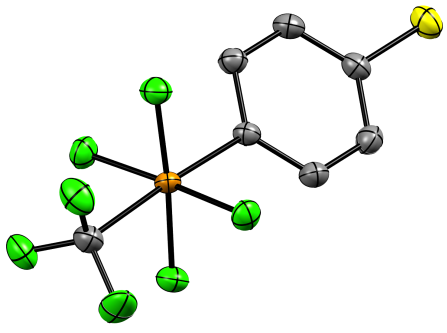
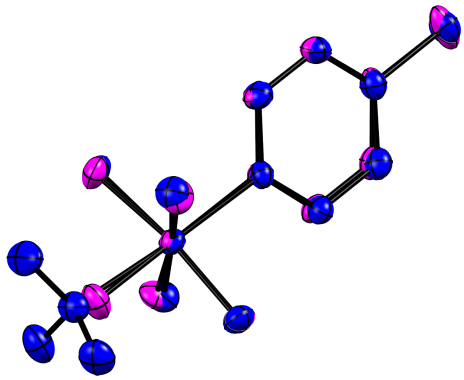
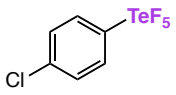
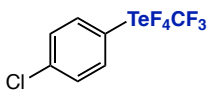


Figure 20: ORTEP view of **Te-4b** (displacement ellipsoids at 50% probability level). Hydrogen atoms are omitted for clarity.

of ^{3}J(F-F) = 22 Hz. Or course again ^{125}Te satellites appear with a ^{1}J(Te–F) of 3341 Hz and ^{2}J(Te–F) 1059 Hz. The ^{125}Te signal, again a broad singlet, appears at δ = 757 ppm. Infrared spectroscopy revealed a significant difference between aryl-TeF_5 and aryl-TeF_4CF_3. The asymmetric stretching vibration of the latter experiences a strong red shift to 625 cm^{-1} (from 655 cm^{-1} in **Te-2a**), indicating weaker Te–F bonds in the latter. As mentioned above, crystals suitable for X-ray diffraction could be grown for **Te-4b** by slow evaporation of a solution of the compound in MeCN. To put the solid-state structure of **Te-4b** into perspective, its collected XRD data was subsequently compared to the crystal structure of pentafluoro analogue **Te-2d**. Compound **Te-4b** exhibits a distorted octahedral geometry similar to **Te-2d**, although with an angle $\theta(C–Te–CF_3)$ = 176.88 thus more significantly deviating from linearity. Furthermore, the average angle $\theta(C–Te–F_{eq})$ of 92.88° is much closer to the ideal angle of 90° than the corresponding angle in **Te-2d** (94.2(3)°). Moreover, the C_{ipso}–Te bond lengths of **Te-4b** and **Te-2d** of 2.061(4) Å and 2.057(4) Å, respectively, are similar. Notably, the Te–CF_3 bond is 2.185(5) long and thus more than 6% longer than the Te–C_{ipso} bond in the same molecule, which is most likely a result of both, sterics of the somewhat bulky CF_3 group and hybridization (Te–C(sp^3) vs. Te–C(sp^2)). Standing out are the Te–F_{eq} bonds in **Te-4b** which are slightly longer (2% difference, i.e. average **Te-4b**: d(Te–F_{eq}) = 1.889 Å, vs. average **Te-2d**: d(Te–F_{eq}) = 1.853 Å)), which is consistent with the observed redshift of **Te-4b** in the acquired IR data. For an improved visual comparison, a structural overlay of compounds **Te-2d** and **Te-4b** was generated and is depicted in Figure 21, together with an overview over the most important structural parameters.







Bonds	*Angle (°)*
F_{eq}-Te-F_{eq}	89.7*
F_{ax}-Te-F_{eq}	85.83(3)
F_{ax}-Te-C_{ipso}	180.0

Bond	*Bond Length (Å)*
Te-F_{ax}	1.827(2)
Te-F_{eq}	1.853(1)
Te-C_{ipso}	2.057(4)

Bonds	*Angle (°)*
F_{eq}-Te-F_{eq}	89.9*
F_{eq}-Te-CF_3	87.2*
C_{ipso}-Te-CF_3	176.8(2)

Bond	*Bond Length (Å)*
Te-CF_3	2.185(5)
Te-F_{eq}	1.889*
Te-C_{ipso}	2.061(4)

Figure 21: **Top**: Molecular overlay of **Te-2d** (pink) and **Te-4b** (dark blue).
Bottom: Overview of the most important bond lengths and angles in the two molecules

3.2.7 Structural Considerations – SF_5 versus TeF_5

In the next step the size and structure of the TeF_5 group are put into perspective by comparison with well-known functional groups, especially SF_5 and to a lesser degree CF_3. Thereby, a qualitative analysis of the molecular volumes of these groups should become possible. To that end, firstly the molecular structures of **Te-2j** and **Te-2m** are examined in juxtaposition with their SF_5 congeners **S-4h** and **S-4i** (Figure 22).

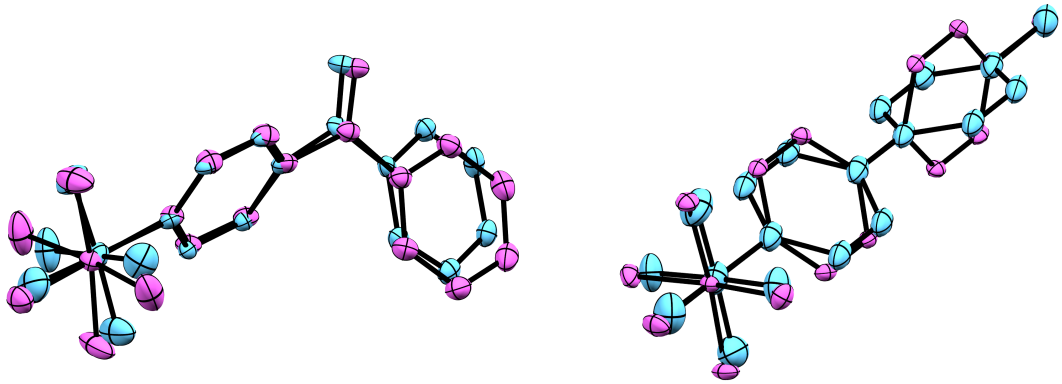


Figure 22: **Left**: Molecular overlay of **Te-2j** (purple) with **S-4h** (blue)
Right: **Te-2m** (purple) with **S-4i** (blue).

Focusing on species **Te-2j** and **S-4h** first, it is evident that the angles around the central chalcogen atom are very comparable between both species (Figure 22, left) with $\theta(C–Te–F_{ax})$ = 179.0(1)°, $\theta(F_{eq}–Te–F_{eq})$ = 89.7(1)°, $\theta(F_{eq}–Te–F_{ax})$ = 85.6(1)° and $\theta(C–S–F_{ax})$ = 178.1(2)°, $\theta(F_{eq}–Te–F_{eq})$ = 89.1(2)°, $\theta(F_{eq}–Te–F_{ax})$ = 87.6(2)°. However, it is also apparent that the chalcogen–F bond lengths in both species vary significantly. The Te–F bonds ($d(Te–F_{ax})$ = 1.835(2) Å and $d(Te–F_{eq})$ = 1.848(2) Å) as well as the Te–C bond (d(Te–C) = 2.077(2) Å) are generally longer than the analogous bonds **S-4h** ($d(S–F_{ax})$ =1.569(4) Å, $d(S–F_{eq})$ =1.562(4) Å and d(S–C) = 1.787(5) Å). Similar structural differences can be extracted from the X-ray data of **Te-2m** and **S-4i** (Figure 21, right). Again, the angles are in very close agreement between both species with $\theta(C–Te–F_{ax})$ = 179.2(1)°, $\theta(F_{eq}–Te–F_{eq})$ = 91.1(1)°, $\theta(F_{eq}–Te–F_{ax})$ = 86.1(1)° and $\theta(C–S–F_{ax})$ = 178.6(2)°, $\theta(F_{eq}–S–F_{eq})$ = 90.4(2)°, $\theta(F_{eq}–S–F_{ax})$ = 88.8(2)°. Moreover, the Te–F distances are comparable to the corresponding bonds in **Te-2j** with $d(Te–F_{ax})$ = 1.832(2) Å and $d(Te–F_{eq})$ = 1.862(2) Å) and a Te–C bond length of 2.068(2) Å. Again, the S–F bonds in the sulfur congener $d(S–F_{ax})$ = 1.549(5) Å and $d(S–F_{eq})$ = 1.590(2) Å are significantly shorter. The same is true for the S–C bond d(S–C) = 1.795(5) Å.

Note, in comparison to their tellurium counterparts, the equatorial S–F bonds are longer than the axial bonds within the same molecule, the opposite is the case for Te–F bonds, this observation could be a reason why equatorial Te–F bonds tend to break more easily, as seen in aryl-TeF_5 derivatization reactions (see above).

With the XRD data in hand, it was possible to assess the relative molecular volume (V_M) of the TeF_5 groups in **Te-2j** and **Te-2m** by comparison to the SF_5 groups in **S-4h** and **S-4i** (inspired by reports that have compared the volume of the SF_5 and CF_3 groups).[138,139] To this end, three common methods were used and compared. All three methods rely on theoretical calculations (to varying degrees) and their numerical results should always be taken with a grain of salt. They allow, however, a more intuitive understanding of the «size» of TeF_5 and are shortly described below.
The first method requires simple arithmetics and its calculation follows the simple formula shown in Equation 1:

$$\frac{V_{m1}}{Z_1} - \frac{V_{ref}}{Z_{ref}} = \Delta V_m \qquad (1)$$

V_{m1} is the molecular volume of all molecules in the unit cell and Z is the number of molecules per unit cell. As this method only gives a difference in molecular volumes (ΔV_m) between two different species, it requires a reference molecule. The relative comparison of molecular volumes of different species is then done with respect to the "baseline volume" (V_{ref}) of the reference molecule. As a reference for the determination of volumes of different functional groups typically the unsubstituted or "hydrogen substituted" species is chosen (i.e. benzophenone in the case of **Te-2j** and **S-4h**). However, the method works with the following assumptions that deduct from its accuracy:
i) Hydrogen atoms can be considered spherical, and have the van der Waals volume of V_{vdW} = 7.2 Å^3; ii) atoms and bonds occupying equivalent positions in two similar molecules (i.e. atoms and bonds other than those in the functional groups in question like the O atom in **Te-2j** and **S-4h**) are not influenced in their volumes and bond lengths by the change of functional groups (i.e. from TeF_5 to SF_5) and iii) packing effects can be ignored.

The second method, using the so-called "Promolecule" approach, is slightly more sophisticated than the first one. It uses the coordinates of the atoms in the functional group (obtained from the XRD measurement) as input and, using the van der Waals radii of said atoms, calculates a molecular volume of the functional group in question. The obvious and erroneous assumption involved in this method is that all atoms, independently of their bonding situation, occupy volumes corresponding to their van der Waals radii.

Finally, the third method, called "Hirshfeld method", uses Hartree-Fock level DFT calculations in combination with the atom coordinates to estimate the atomic volumes and thus the volume of the functional group that is investigated. Naturally, H-F-level calculations are typically no perfect representation of reality and thus also not extremely accurate.

The results from the three different analyses are reported in Table 14. Even though absolute values vary significantly when different methods are compared, the relative volumes of the groups are in fairly good agreement. According to our calculations the SF_5 group, sometimes labeled "super CF_3" is, depending on the method used, 1.5–1.6 times larger in volume than ("non-super") CF_3, which is in line with the literature and places the SF_5 group just slightly below the *tert*-butyl group.[46,139,140] Extending the approach to tellurium, it was also possible to reveal that TeF_5 is ca. 1.2–1.5 larger than SF_5.

Table 14: Summarized results from the theoretical volume analysis of TeF_5.

Substituent	*V_1/Z_1-V_2/Z_2 (Å^3)*[a]	*Hirshfeld (Å^3)*[b]	*Promolecule (Å^3)*[b]	*relative size*[d]
CF_3	39.2[c]	47.9	44.0	1.0
SF_5	62.6[c]	75.7	66.5	1.5—1.6
TeF_5	**95.1[c]**	**92.6[d]**	**82.5[d]**	**1.9—2.4**

[a]Referenced to unsubstituted benzophenone molecular structure to obtain initial value for CF_3, assuming a spherical hydrogen atom with V_{vdW} = 7.2 Å^3. [b]Calculated using Crystal Explorer. [c]Determined by comparing molecular structures with same benzophenone core. [d]Determined for benzophenone derivative. Volume compared to CF_3.

In summary, it can thus be concluded that the TeF_5 group is a functional group considerably larger than CF_3, SF_5 and tert-butyl, alike. The combination of its presumably high lipophilicity with the large steric demand puts it in a unique position for still unexplored applications.

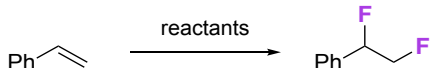
3.2.8 Reactivity and Stability of Pentafluoro(aryl)-λ^6-tellanes

Beyond the structural and spectroscopic properties, the reactivity of the TeF_5 group was also investigated. Since the first experiments by Janzen[130] and Stang[105] in the years 1988 and 1998, the further development of this chemistry had progressed only slowly. As mentioned above, the known reactivity was therefore limited to hydrolysis reactions and, interestingly, to the use of $PhTeF_5$ as a reagent for the vicinal difluorination of olefins. For a better understanding of the reactivity of the aryl-TeF_5 compounds it was necessary to retest the already known properties of these compounds and to reproduce literature results. Initially, we therefore focused on the hydrolysis of $PhTeF_5$ by an excess of water as

described by Janzen. The observations made were identical to those described in 1988.[130] $PhTeF_5$ (**Te-2a**) is bench stable for an extended period of time. It was left in an open borosilicate vial for months (in some cases even over a year), typically stored at low temperature, without any sign of degradation. The majority of crystallizations were carried out in vials open to air without any further precautions and also did not reveal any form of decomposition. $PhTeF_5$ is in fact stable enough to endure flash column chromatography without the occurrence of any major decomposition. The situation is, however, different when $PhTeF_5$ is dissolved in MeCN and subsequently treated with an excess of water. Under these conditions, $PhTeF_5$ undergoes a rapid hydrolysis reaction leading to the formation of *cis*-$PhTeF_4OH$. The ^{19}F NMR spectrum is also congruent with that published by Janzen. Furthermore, the significantly slower, stepwise hydrolysis by exchange of further F atoms could be confirmed. Subsequently, the experiments were also repeated with $PhTeF_4CF_3$ (**Te-4a**). Interestingly, the compound showed a very similar behavior to **Te-2a**. First, only one F atom is exchanged and the compound is converted to *mer*-$PhTeF_3(OH)CF_3$. Further hydrolysis steps are only observed over prolonged reaction times, happen stepwise and each following step takes significantly longer than the prior one. As the ^{19}F NMR was not conclusive and no crystals suited for X-ray diffraction could be grown, the final hydrolysis product of the reaction could not be characterized.

Hereafter the purported fluorination properties of **Te-2a** described by Stang *et al.* were tested.[105] Therefore, isolated **Te-2a** that was prepared by reaction of Ph_2Te_2 with TCICA/KF was reacted with styrene. Surprisingly, however, no reactivity was observed and the olefin and **Te-2a** could be reisolated from the reaction mixture by column chromatography without loss of material. To exclude all eventualities, the reactions were carried out multiple times, in different solvents (DCM and MeCN), at different temperatures (up to 81 °C) and over different time periods (hours to days). The result, however, did not change and reactivity was not observed in any case. After verifying these results, which are contradictory to the literature, the reactivity of **Te-2a** was further investigated in a series of control experiments. Firstly, the reactivity of styrene with **Te-2a** was investigated when the literature method for the synthesis of **Te-2a** was applied. In this case, Ph_2Te_2 was reacted with XeF_2 (5 equiv.) in DCM for 1 h and to the crude product was added styrene. In this case it was possible to observe difluorination and hence reproduction of the literature result albeit in a significantly lower yield of (1,2-difluoroethyl)benzene (3%). Notably, (1,2-difluoroethyl)benzene (and all other reported products of a putative difluorination with phenyl-TeF_5) would also be the expected products of a reaction with XeF_2 alone. Hence, the reaction of styrene with 5 equiv. of pure XeF_2, was examined. As expected, (1,2-difluoroethyl)benzene was obtained in a yield of 70%.

To exclude the possibility that minor amounts of XeF_2 could function as a catalyst in the difluorination of olefins by $PhTeF_5$, styrene was reacted with $PhTeF_5$ (1 equiv.) (synthesized by the TCICA/KF approach) and catalytic amounts of XeF_2 (0.3 equiv.). Less surprisingly, the reaction resulted in poor yield (14%) and catalytic activation of $PhTeF_5$ by XeF_2 can thus be ruled out. Hence, it is a very likely deduction that the reported difluorinating properties of $PhTeF_5$ are due to residual XeF_2 in the used batch of telluride. Evaluating the results of the control experiments allows the conclusion that, in contradiction to what is reported in the literature, $PhTeF_5$ is *NOT* a competent difluorination reagent for olefins and instead far more stable than believed earlier. The results are summarized in Figure 23.



entry	*Ph_2Te_2*	*Ph-TeF_5*	*XeF_2*	*styrene*	*yield (%)*
1	1	0	5	2	3
2	0	0	1	1	70
3	0	1	0.3	1	14
4	0	1	0	1	0

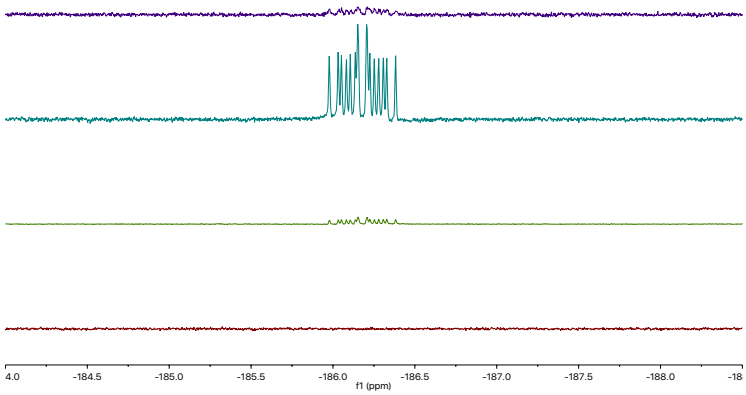


Figure 23: **Top**: Summarized results for the control experiments of styrene with XeF_2 and **Te-2a**.
Bottom: ^{19}F NMR spectra for entries 1-4 in that sequence. The displayed spectra show a dddd (^1J = 49.5, 29.1 Hz and ^2J = 21.0, 15.3 Hz) coupling pattern for the alpha-F-atom at -186.23 ppm.

Besides the investigation of the hydrolytic stability and difluorinating properties of **Te-2a**, the latter has also been treated with a number of nucleophiles in order to further explore its chemistry. Already reported knowledge about the reactivity includes reactions with alcohols, secondary amines, and azides as reported during the last decades. In this case, however, the reported reactivity could be confirmed. For these reactions, $PhTeF_5$ was typically treated with an excess of the corresponding nucleophile. Primarily *cis*-isomers of a mono-substitution reaction of an equatorial fluorine atom by the nucleophile were formed

in each case. This is consistent with our structural observation that Te–F_{eq} bonds are, on average, longer and likely weaker than Te–F_{ax} bonds.
In an attempt to expand upon these reports, reactions of **Te-2a** with a variety of additional nucleophiles (e.g. KCN, tBuNC, $AgSCF_3$, KSCN, PhLi, and MeLi) were also examined. **Te-2a** was treated with the respective nucleophile in MeCN, DCM or THF at various temperatures and for varying time periods, only to reveal that **Te-2a** remains completely intact, which can be seen as another indication of its relative chemical inertness.
From another perspective, we also examined the behavior of **Te-2a** in the presence of TMSX reagents (e.g. X=CF_3, CF_2H, CF_2CF_3, CN, and acetylide) – with and without CsF – and observed no reactivity.
In a final effort to overcome this "sluggish" chemical behavior, an array of photochemical reactions was conducted. Therein, the reactivity of **Te-2a** with a number of substrates under 300 nm UV irradiation in MeCN for 16 h was investigated, both in the presence and absence of sensitizers. Unfortunately, however, in all cases, **Te-2a** is ostensibly unreactive.
In a final statement about **Te-2a** it can be concluded that the greasy, highly lipophilic, larger congener of SF_5 is much more reactive than its counterpart, but at the same time not nearly as unstable as previous literature accounts had us believe.

The results for the reactivity screenings under i) the addition of nucleophiles and olefins and ii) photochemical conditions are summarized in the appendix.

3.2.9 Additional Experiments with Monotellurides

Having explored the reactivity of ditellurides with TCICA/KF we came across reactivity of similar species that we hadn't intended to investigate at first, monotellurides.
Whilst working on ditellurides as described above, we synthesized a variety of differently substituted diaryl ditellurides, typically analyzing those starting materials by means of NMR spectroscopy. We were, however, not aware that during the reaction of aryl Grignard reagents with elemental tellurium, also monotellurides can be formed. Thus, upon completing the synthesis and purification by column chromatography of putative bis(3-fluorophenyl)ditelluride, the compound was analyzed by ^{19}F and ^{1}H NMR spectroscopy. Both spectra revealed the presence of only one NMR active species and the conclusion was that we had obtained pure ditelluride, as in all previous cases. Thus, we proceeded to react the newly obtained telluride with TCICA/KF and analyzed the crude reaction mixture by ^{19}F NMR. Surprised that a broad singlet instead of the typical TeF_5 pattern (doublet and pentet) along with a singlet for the aromatic F atoms was observable, at -55.58 ppm, we deducted, still under the assumption of having worked with a ditelluride starting material, that the product was possibly an oxotrifluoro derivative.

The integration of the NMR spectrum revealed a ratio of aromatic F to Te–F atoms of ca. 1:2.5, leading us to misjudge the chemical composition of the product. To gain more insight into this reaction, the compound was purified and left to crystallize from *n*-hexane. To our great surprise, the XRD data revealed an unexpected structure (Figure 24). The formation of this specific monotelluride instead of the expected ditelluride can be likely attributed to an incomplete formation of aryl-Grignard reagent. Thus, leftover 3-fluoroiodobenzene may have reacted in a nucleophilic aromatic substitution with the preformed strongly nucleophilic aryl-tellurolate. However, this hypothesis has not been investigated further and repetition of the experiment with excess magnesium yielded ditelluride only. In contrast to the TeF_5 structure reported above, XRD data for *trans*-Ph_2TeF_4 had previously been collected by Klapötke *et al.*[131] Due to the molecules high symmetry the Te–F bonds are equivalent and show bond lengths very similar to the previously reported structures with a distance d(Te–F) of 1.900(3) Å and a d(Te–C) bond length of 2.082(3) Å. The structure is nearly perfectly octahedral with a nearly linear θ(C–Te –C) bond angle of 177.4(2)°, θ(F–Te –C) angles of 89.5(2)° or 91.3(2)° and θ(F–Te –F) having values of 179.1(2)° and 180.0(2)°. It was a pleasant surprise that the TCICA/KF approach could also be applied to diaryl monotellurides to convert them into their corresponding tetrafluorinated derivatives. This discovery combined with the synthetic procedures by Zhang, enabling facile access to R_2Te monotellurides could open up the almost entirely unexplored field of the chemistry of diaryl-TeF_4 species.[141] Due to time constraints, a project idea in this direction could not be carried out as part of this thesis and remains to be explored.

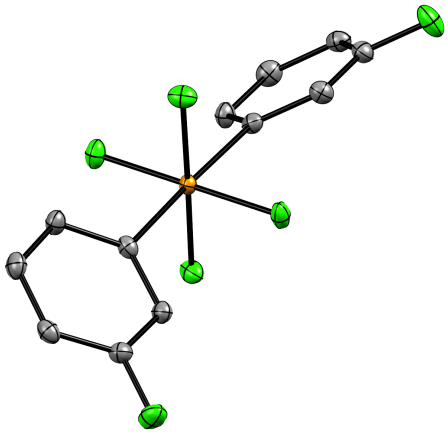
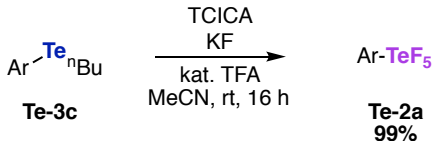


Figure 24: ORTEP view of *trans*-bis(3-fluorophenyl) telluride (displacement ellipsoids at 50% probability level). Hydrogen atoms are omitted for clarity.

Finally, a short reactivity study of organo(mono)tellurides under oxidative fluorination conditions was less coincidental. We had suspected that the application of TCICA/KF to aryl-Te-alkyl species leads to the cleavage of the alkylic C–Te bond. With this idea in mind, we tested the reactivity of the related tellurium derivative PhTe^{n}Bu (**Te-3c**, Scheme 6).



Scheme 6: Possible synthetic route to phenyl-TeF_5 from phenyl(*n*-butyl)telluride and TCICA/KF.

The synthesis **Te-3c** was achieved following a method published by Perin *et al.*[142] Therefore $^{n}Bu_2Te_2$ (obtained by treatment of Te metal with ^{n}BuLi) was treated with $PhB(OH)_2$ and oxone in dry EtOH at 60 °C for 5 h. Purification was achieved by column chromatography giving the monotelluride **Te-3c** in 80% yield as a yellow oil. The purified **Te-3c** was subsequently treated with TCICA/KF. The resulting reaction was violent and started immediately upon addition of the oxidant. An increase in temperature to at least 82 °C (boiling point of MeCN) was observed and the color quickly faded from yellow to colorless. After 24 h, a ^{19}F NMR with an internal standard (trifluorotoluene) was measured and a ^{19}F NMR yield of >99% for $PhTeF_5$ was determined. This certainly leads to the conclusion that C–Te bond activation takes place in the case of aryl-alkyl monotellurides and that the tellurium species is converted to its TeF_5 derivative. This discovery should permit even more facile synthetic access to a variety of aryl-TeF_5 compounds. Accessing some ditellurides, especially such containing strongly electron-withdrawing substituents, can be unforgiving as the preparation of the corresponding aryl-Grignard or aryllithium species is not always straightforward. On the other hand, synthetic access to $^{n}Bu_2Te_2$ is possible in high yields and the necessary aryl-boronic acids are cheap and their chemistry, due to their widespread application in cross-coupling chemistry, is well known. Thus, future chemists should have an interesting opportunity to further develop $RTeF_5$ chemistry from relatively common and easy to handle starting materials in combination with TCICA/KF.

3.3 Conclusions and Outlook

A series of pentafluoro(aryl)-λ^6-tellanes was successfully synthesized using a novel and mild approach for the oxidative fluorination of diaryl ditellurides. The compounds were extensively characterized by means of NMR and IR spectroscopy and mass spectrometry. Furthermore, the first crystal structural data of aryl-TeF_5 compounds was obtained. Comparison of the latter with analogous X-ray data of the congener aryl-SF_5 allowed for an in-depth analysis of the structure and geometry of both groups and helped to put the relative size of the TeF_5 group into perspective. The methodology was also extended to the synthesis and structural study of heretofore unknown aryl-TeF_4CF_3 compounds. Additionally, "known" reactions of the compound class were repeated and those preliminary reactivity studies unveiled some inconsistencies with previous literature regarding $PhTeF_5$. While the reported hydrolysis of the group upon contact with water, as well as its reactivity with a variety of nucleophiles could be confirmed, its supposed difluorinating properties were refuted as likely attributed to remaining XeF_2 in the sample reported in the literature procedures. In conclusion, it can be safely said that although the aryl-based TeF_5 (and TeF_4CF_3) group is not quite as robust as the SF_5 group, it is more stable than previously thought, thus opening a door to explore new applications of this motif. Furthermore, future access to TeF_5 compounds could be achieved by treatment of dialkyl tellurides under TCICA/KF conditions, thereby potentially facilitating the development of TeF_5 chemistry further. However, the evaluation of this new reaction has yet to be carried out. Finally, our TCICA method enabled new access to the still largely unexplored but remarkably stable R_2TeF_4 class of compounds.

Chapter 4

Organophosphorus(V) Fluorides and their Salts: History, Application and Facile Synthesis

Parts of this chapter are published and have been adapted with permission from:

«Deoxygenative Fluorination of Phosphine Oxides: A General Route to Fluorinated Organophosphorus(V) Compounds and Beyond» **Dustin Bornemann**, Cody Ross Pitts, Lionel Wettstein, Fabian Brüning, Sebastian Küng, Liangyu Guan, Nils Trapp, Hansjörg Grützmacher,* and Antonio Togni*, *Angew. Chem. Int. Ed.* **2020**, *Just Accepted.* DOI: 10.1002/anie.202010943

4.1 Introductory Remarks

As in the previous chapters, the first part of the following section is meant to „set the mood“ and introduce the reader to the general topic of phosphorus and its chemistry. Emphasizing the impact that the sheer discovery of the element had on people living at the time, an excerpt of the German poem “Phosphorus Mirabilis” is cited below:

«Wer seine Natur nicht näher kennt,
Der fürchtet im Dunkeln, daß er brennt;
Indessen man kann ihn gefahrlos berühren,
Von seinem Feuer ist nichts zu spüren.»

The lines above are from the pen of none other than the father of differential calculus, Gottfried Wilhelm Leibniz, and those are but a few of the ardent phrases used to describe element 15, phosphorus. In order to understand the early fascination with the pentel, its history shall be explored briefly. A detailed discussion of phosphorus fluorides, their discovery, major developments and state-of-the-art research in the field of organophosphorus(V) fluorides and their salts will follow.
For further reading on the element in general the insightful article “A brief history of Phosphorus”[143] by Ashley *et al.* and Emsley’s book “The 15th Element”[144] are recommended.

4.2 Introduction

4.2.1 Phosphorus in the Historical Context

Although far more abundant than sulfur, which has been known and used by humankind for millennia, the pentel phosphorus was discovered less than 400 years ago.[5] Before the dawn of modern chemistry, German alchemist Hennig Brand stumbled over the element in his search for the mythical Philosophers Stone in 1669.[143,144] Having distilled large amounts of urine (supposedly 50 buckets), Brand discovered that, upon completion, his procedure led to the formation of a white, solid residue. When subjected to air, the chunk reacted with the atmosphere, glowing faintly in the dark.[144] Unbeknownst to him at the time, he had just discovered elemental, white phosphorus, and along with it the first chemiluminescent system (Figure 25). The occurring reaction transforms elemental phosphorus upon contact with moisture and oxygen to HPO and P_2O_2, both short-lived molecules that, upon prior excitation, emit light in the visible spectrum, which

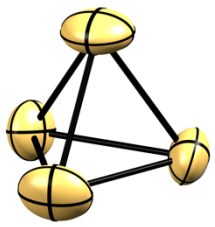


Figure 25: ORTEP view of white phosphorus exhibiting tetrahedral geometry (displacement ellipsoids at 90% probability level).

has only been understood in 1976.[145] It was the emission of this faint glow that gave the element its name "phosphorus" after the Greek term phōsphóros for light-bringer.
Even though his quest for the Philosophers Stone wasn't fruitful, Brand had secured his place in history, becoming the first human to discover a new element since ancient times. However, the nature of phosphorus as an element was only realized a century later by Lavoisier who published his work on chemical nomenclature and elements in 1789.[146]
The extraordinary properties of the *mysterious light-bringer* or "phosphorus mirabilis" fascinated and inspired scientists like Boyle and Leibniz as well as painters like Joseph Wright of Derby. The latter even dedicated his famous painting *The Alchemist Discovering Phosphorus* (Picture 3) to the element and its discoverer.[143,147] But it was not until much later that the importance of this discovery for life and thus by proxy, industry, was truly understood. While initial applications of the element still focused on its entertaining luminescent and its supposed health-promoting properties, the latter mainly advocated by numerous quacks at the time, its uses changed over time along with the means of its production and the understanding of its properties.[144] In the decades following its discovery, Brand's method that relied on urine, although slightly improved by Boyle, remained the main source of elemental phosphorus and was, with an annual production of a few kilograms in the late 17th century, too inefficient to allow for mass production and thus the use in any form of industry.[144] The situation changed dramatically when Johan Gottlieb Gahn and Carl Scheele discovered calcium phosphate in bones in 1769.[144] Animal bones and bone ash were abundant and the relative phosphorus content in them much higher than in urine, increasing the efficiency and lowering the cost at which the isolation of the pentel could be achieved.

Picture 3: Joseph Wright of Derby's famous painting titled: *The Alchemist Discovering Phosphorus* from 1771, after Brand's discovery of white phosphorus.

This spawned the first phosphorus-based industry, dealing with the isolation of the element for research purposes and the production of phosphorus-based goods, most notably the first fertilizers and matches. It was the discovery of the latter that helped develop a growing market for the element and as a consequence increased demand and production for it to over 500 tons in 1881. Another breakthrough happened in 1870 when Albright and Wilson discovered that the abundant, easy to mine guano could be used as a surrogate for bones, which as a consequence dominated the phosphorus market as a resource until the late 19th century. The final advance towards modern phosphorus mining came in 1888. The

electrical arc furnace was developed by Readman and along with it, mining of phosphorus-containing rocks became the main source of phosphorus, which still holds true nowadays.[148] Thus, the most significant global source of phosphorus is phosphorite, a sedimentary rock with varying contents of phosphate minerals. In 2019 the annual production of phosphate rock was 240 million tons, more than 90% of which are burned to phosphorus pentoxide, P_4O_{10}.[149,150] The pentoxide is subsequently used by various industrial sectors for the production of phosphoric acid and salts thereof, which are predominantly applied as detergents and fertilizers. Especially the latter application of phosphorus makes it essential for the modern agricultural industry. A minor amount of the global phosphorus production is applied in the production of phosphorus chlorides and other inorganic and organic phosphorus species.[149]

4.2.2 Phosphorus Fluorine Chemistry – Remarks

With the rise of the phosphorus industry came the interest of scientists in its chemistry. It is, similar to the case of sulfur, a difficult task to summarize all relevant phosphorus chemistry of the last few centuries within the scope of a single doctoral thesis, as the field is simply too vast. However, as compounds bearing fluorinated heteroatoms like fluorophosphines, -phosphoranes, -phosphates or phosphonium fluorides are the main focus of this thesis, the next subchapters will introduce phosphorus fluorine chemistry and attempt to give a general overview about its most fundamental compounds and their chemistry.

4.2.3 Homoleptic Phosphorus Fluorides

The substance class of phosphorus halogenides contains a plethora of fluorohalides (e.g. $PBrF_2$), polyhalogenides (e.g. $[PBr_4]Br_3$) as well as homoleptic halides (e.g. PCl_3) including fluorides (e.g. PF_5) and more.[149] Focusing on the latter reveals that there are three molecular, homoleptic phosphorus fluorides and salts thereof that constitute the main body of inorganic phosphorus fluorine chemistry. Bearing phosphorus in the oxidation state +II, phosphorus difluoride or P_2F_4 is among the low-valent phosphorus halogenides. The compound can be accessed by reduction of PF_2I with elemental mercury as first demonstrated by Rudolph *et al.* in 1966.[151] It is infrequently used in photochemical reactions of alkenes and alkynes, resulting in the addition of difluorophosphino groups at each side of the C–C multiple bond.[152]

The trivalent PF_3 was the first fluoride of phosphorus to be discovered. Our old acquaintance Henri Moissan discovered the compound in 1884 when he treated PCl_3 with AsF_3 obtaining a colorless, toxic gas in the process. The modern synthesis of PF_3 is typically achieved by treatment of PCl_3 with ZnF_2.[149] Unlike its chlorinated counterpart PCl_3, PF_3 is significantly more stable, decomposing only slowly when in contact with water. The trifluoride, however, does not have any industrially relevant applications, although the compound is employed in academia as a ligand in transition-metal chemistry where it can be used as a surrogate for carbon monoxide (Figure 26).[153]

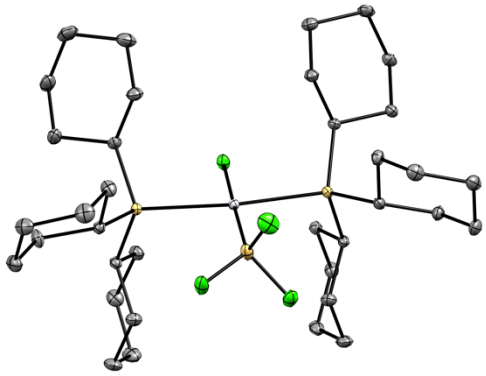


Figure 26: ORTEP view of trans-$[(Cy_3P)_2PtF(PF_3)]^+$ as reported by Arnold et al. Hydrogen atoms, counteranions and solvent molecules omitted for clarity (displacement ellipsoids at 50% probability level).

Finally, the highest-valent, homoleptic fluoride is phosphorus pentafluoride, PF_5. The compound was discovered by Thomas E. Thorpe in 1876. Analogous to Moissan, Thorpe treated the pentachloride PCl_5 with AsF_3, obtaining the gaseous pentafluoride in the process, a procedure still applied today.[149,154] Although the compound is a relatively strong Lewis-acid, industrial and academic applications of PF_5 itself are limited (it is scarcely used in organic chemistry as a fluorinating reagent). The situation is, however, radically different for derivatives of the compound, most notably for the hexafluorophosphate anion, PF_6^- (Figure 27). Hexafluorophosphate salts like $LiPF_6$ are of utmost importance for modern life as they constitute a major component of electrolytes in lithium-ion batteries, which are heavily used in modern mobile phones or other portable electronic devices.[155–157] Apart from the obvious economic role such devices play, their impact on society and science was great enough that the 2019 Nobel Prize in chemistry has been awarded to the chemists J. B. Goodenough, M. S. Whittingham and A. Yoshino who advanced the field considerably. Next to their use in batteries, academic applications of the hexafluorophosphate anion are frequently centered around its utility as a stable, non-coordinating counterion in complex chemistry as well as in ionic liquids. The phosphate, being isoelectronic to SF_6, exhibits an octahedral geometry with six equivalent P–F bonds, and is, similar to sulfur hexafluoride, chemically rather robust. While decompositions of the PF_6^- anion have been reported, they require either relatively harsh conditions to occur and are often kinetically inhibited, so the

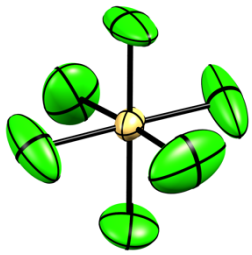
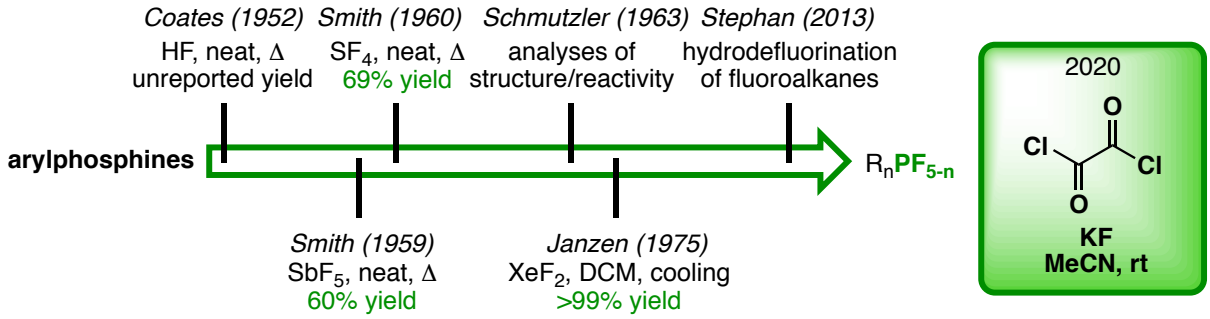


Figure 27: ORTEP view of PF_6^-. Counteranions omitted for clarity (displacement ellipsoids at 50% probability level).

compound is nonetheless frequently used as a (semi-)inert counterion in chemistry.[158,159] Interestingly, in contrast to the developments of inorganic chemistry, organic PF_5 chemistry still is considerably lacking. This fact becomes apparent when considering that it was not until the late 1950s and early 1960s that chemists explored the field of organic phosphorus fluorine chemistry for the first time. This field and the compound class of organophosphorus(V) fluorides are of particular interest within the scope of this thesis and therefore, the next subchapters will revolve around the historical development of those organic phosphorus fluorides and their chemistry.

4.2.4 Organophosphorus Fluorine Chemistry – Timeline

Derived from PF_5 chemistry is the field of organophosphorus fluorine chemistry. Of relevance for this thesis is a particular subset of compounds in this substance class, namely aryl- and alkylphosphorus(V) fluorides and derivatives thereof. In contrast to general phosphorus fluorine chemistry, industrial as well as academic applications or physical and chemical properties of organofluorophosphoranes are much less explored. A plausible explanation for this finding is that the field is only ca. 60 years old and, furthermore, the chemistry used to explore organophosphorus fluorine chemistry frequently relied on unforgiving, highly toxic or otherwise dangerous fluorination reagents like HF, F_2 or SF_4, which require a sophisticated infrastructure and know-how for safe handling or otherwise considerably expensive reagents like XeF_2.



Scheme 7: Timeline with important developments in arylphosphorus fluorine chemistry.

Scheme 7 provides a short historical overview of the notable development and major breakthroughs of organophosphorus fluorine chemistry and its applications.

4.2.5 Organophosphorus Fluorine Chemistry – The Early Days

The first access to an organophosphorus(V) fluoride was achieved by Coates and Carter in 1952. The duo was able to synthesize $MePF_4$ by fluorination of the salt $[MePCl_3][AlCl_4]$ with HF in an autoclave at room temperature.[160] The authors state that their process would, in principle, also be applicable to derivatives of the type $[RPCl_3][AlCl_4]$, yielding RPF_4 in the process. Unfortunately, no yields or detailed analyses are given in the patent literature, but the authors comment on the stability of said compounds, stating that they are prone to rapid hydrolysis, forming $RP(O)(OH)_2$ when subjected to moisture.

Following their initial publication, several methods concerning the synthesis of analogous compounds of the general composition R_nPF_{5-n} have been published, all applying in principle one of three different synthetic routes.

Firstly, Komkov *et al.*, in analogy to Coates and Carter, fluorinated $[RPCl_3]^+$ and $[RPCl_4]$ species by treatment with HF, AsF_3 or SbF_3 in 1962.[161] Primary literature for these syntheses can unfortunately not be accessed in English and thus no detailed information about the described processes can be provided. The second route to R_nPF_{5-n} species was patented by Smith in 1959.[162] This patent marks the beginning of arylphosphorus fluorine chemistry as Smith described the oxidative fluorination of phenyldichlorophosphine with SbF_5 or, alternatively, oxidative chlorination (e.g. with $SbCl_5$) and subsequent Cl–F exchange with SbF_3. The reaction was carried out at 70–90 °C and the product, $PhPF_4$, was isolated by distillation in up to 60% yield. The publication also describes the synthesis of *n*-octyl and other alkyl-PF_4 species with comparable success. Like his predecessors, Smith also noted that, due to their high Lewis acidity, RPF_4 species are very prone to hydrolysis and thus that reactions have to be carried out under an inert, dry atmosphere. He, however, did not further explore the reactivity of his products. The final route was again described by Smith in 1960.[163] Treating phosphonic acids and phosphonic difluorides in a desoxygenative fluorination reaction with SF_4 (for more information on SF_4 *vide supra*, chapter 2) at 100–120 °C, afforded $PhPF_4$ in up to 62% yield. Interestingly, the procedure was not only applicable to the aforementioned starting materials but also allowed for the synthesis of Ph_2PF_3 from phosphinic acids (i.e. $Ph_2P(O)OH$) in 42% yield and Ph_3PF_2 from either $OPPh_3$ or PPh_3 in 67% or 69% yield, respectively. Smith also diligently analyzed his products by NMR and IR spectroscopy as well as elemental analysis, providing early insight into the spectral properties of these interesting

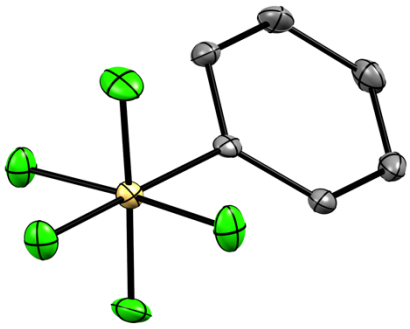


Figure 28: ORTEP view of $[PhPF_5]^-$ as described by Vabre et al. Hydrogen atoms and counteranions omitted for clarity (displacement ellipsoids at 50% probability level).

compounds. A crystal structure of an arylphosphorus(V) fluoride, namely $[PhPF_5]^-$, was only obtained long after its initial synthesis in 2017 by Vabre *et al.* (Figure 28).[164] However, a first in-depth analysis of the spectral, and thus by proxy, structural properties of phosphorus(V) fluorides was carried out by Muetterties and Schmutzler and coworkers in 1963.[165] The group synthesized and collected spectral data of a library of mono-, di-, and trisubstituted phosphorus(V) fluorides. The data was then evaluated in terms of stereochemistry, configurational exchange, and general correlation of spin-spin coupling and chemical shift data, providing the chemical community with a comprehensive spectral overview of dialkyl, diaryl, and alkyl-aryl R_nPF_{5-n} derivatives. A noteworthy result of their work is the realization that all R_nPF_{5-n} species adopt a trigonal bipyramidal structure with the R groups occupying the equatorial positions, leading to the concept of *apicophilicity* described by Muetterties *et al.* in a follow-up publication.[166]

With this analytical data in hand, Schmutzler proceeded with the first experiments regarding the reactivity of R_nPF_{5-n} species. In a publication from 1964, the scientist describes a variety of new phosphorus(V) fluorides together with their analytical data.[167] More interesting, however, is his evaluation of their reactivity towards various carbonyl compounds. The idea was that fluorophosphoranes "[…] *might resemble sulfur tetrafluoride as a fluorinating agent while being liquids which can be handled conveniently* […]", making them an ideal replacement for the extremely hazardous gas. Unfortunately, Schmutzler's results showed that, while carbonyl species do indeed undergo violent reactions with RPF_4 species, the outcome of the reaction is rarely well-defined and leads mainly to the formation of mostly unidentified polymerization side products. The application of fluorophosphoranes as desoxyfluorination reagents never bore fruits and with the development of DAST®, Deoxofluor®, Fluolead® and other, similar compounds (see chapter 2) the reaction type remained firmly within the grasp of sulfur chemistry. A slowing factor in the development of phosphorus(V) fluoride-based reagents was the difficult access of compounds within that class. Nevertheless, Schmutzler remained very active in the field of P(V) fluorides contributing greatly towards the understanding of the physicochemical properties of said compounds. Examples of further contributions include the synthesis of an NHC-P(V) adduct together with Arduengo, the synthesis of heterocyclic fluorophosphoranes, NMR studies on coordination compounds with P–F ligands, and more.[168–170] To honor his numerous contributions to the field of phosphorus fluorine chemistry, *Nachrichten aus der Chemie* recently dedicated an obituary to the late German chemist.[171]

A notable advancement towards more accessible organophosphorus fluorides was made by Janzen and coworkers in 1975. Inspired by the interesting reactivity of XeF_2 with various main group elements as well as organic compounds and metal complexes, the group investigated the oxidative fluorination of phosphines by XeF_2.[172] It was possible to show

that triarylphosphines along with organochlorophosphines can be easily converted into R_nPF_{5-n} species with almost quantitative yields and facile purification upon treatment with XeF_2 at low temperatures (between -196 °C and -10°C). This step towards a solid reagent for the synthesis of R_nPF_{5-n} compounds marked a remarkable improvement over the hazardous, in part gaseous, reagents used in the previous decade and allowed for a much more facile access to compounds of that class. The same year also saw the first crystal structure of an Ar_3PF_2 compound, namely tris-(pentafluorophenyl)difluorophosphorane published by Sheldrick, which clearly showed that the NMR interpretations of Schmutzler, predicting axial fluorine atoms in the trigonal bipyramid, were indeed correct.[173]

However, the initial euphoria of the 1960s with respect to organophosphorus fluorine chemistry did not transfer into the upcoming decades. After the discoveries by Janzen and coworkers, publications in the field became scarce and it was only recently in 2012 when the Stephan group published their article on Lewis-acidic fluorophosphonium ions as potential organocatalysts, that the topic became of broader interest again.[174]

4.2.6 Organophosphorus Fluorine Chemistry – Renaissance in the 21st Century

When Stephan and coworkers discovered the potential of organophosphonium cations derived from organophosphorus difluorides in CO_2 sequestration and hypothesized about their applicability in frustrated Lewis pair (FLP) chemistry, the interest in organophosphorus fluorine chemistry began to reawaken.[174] Stephan's group described the synthesis of difluorinated *ortho*-phosphinoaniline derivatives $Ph_2PF_2(o\text{-}C_6H_4NHMe)$ and $PhPF_2(o\text{-}C_6H_4NHMe)_2$ from $Ph_2P(o\text{-}C_6H_4NHMe)$ and XeF_2 in quantitative yields, following the procedure described by Janzen in the 70s.[172] Deprotonation of the amines using ^{t}BuLi at -78 °C afforded $Ph_2PF(o\text{-}C_6H_4NMe)$ and $PhPF(o\text{-}C_6H_4NMe)_2$ with bidentate, chelating aniline "ligands" coordinated to phosphorus in 89% and 75% yields, respectively. Both compounds could consequently be used in CO_2 sequestration reactions. Interestingly, they also treated both aryldifluorophosphoranes with TMSOTf, a strong

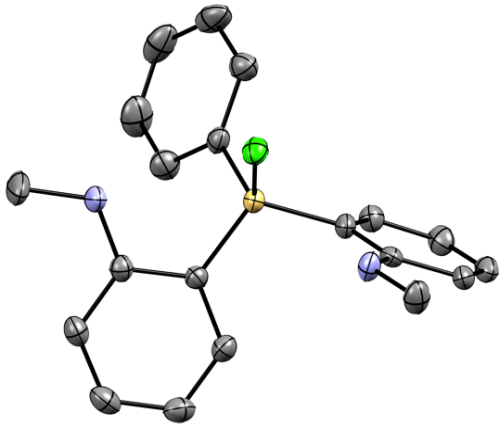


Figure 29: ORTEP view of $[PhPF(o\text{-}C_6H_4NHMe)_2]^+$ as described by Stephan and coworkers. Hydrogen atoms, counteranions and solvent molecules omitted for clarity (displacement ellipsoids at 50% probability level).

fluoride abstraction reagent, yielding the phosphonium fluorides $[Ph_2PF(o\text{-}C_6H_4NHMe)]^+$ and $[PhPF(o\text{-}C_6H_4NHMe)_2]^+$in the process. Both compounds were obtained in good 65% and 70% yields and fully characterized, including XRD-measurements (Figure 29). It was this group of phosphonium cations that should later be the spark finally rekindling the fire of organophosphorus fluorine chemistry.

In order to further increase the Lewis-acidity of their phosphonium fluorides, the Stephan group modified the arenes by substituting them with more strongly electron-withdrawing ones. Thus, in 2013 the group first published the synthesis of a phosphonium cation based on diphenyl(pentafluorophenyl)difluorophosphorane, $Ph_2(C_6F_5)PF_2$.[175] Abstraction of the fluoride was again achieved with TMSOTf but was also shown to be possible using $B(C_6F_5)_3$. The thereby obtained $[Ph_2(C_6F_5)PF]^+$ reacted with PPh_2SiMe_3 and TBAT, forming the mixed-valent species displayed in Figure 30. However, Stephan and coworkers were not yet satisfied. Having discovered these synthetic routes to triarylphosphonium fluorides from arylphosphorus(V) difluorides allowed the group to take the chemistry one step further.

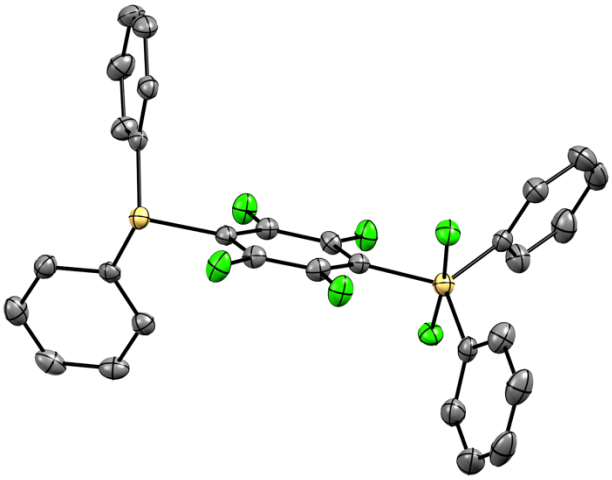
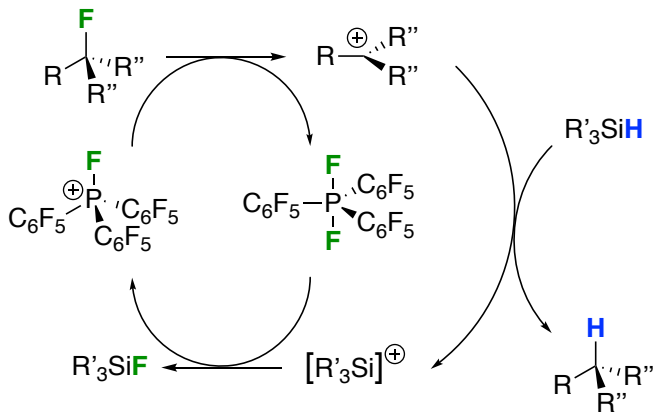


Figure 30: ORTEP view of a mixed-valent arylphosphorus(V) fluoride as described by Stephan and coworkers. Hydrogen atoms omitted for clarity (displacement ellipsoids at 50% probability level).

So, they aimed for even more Lewis-acidic species and thus synthesized tris(pentafluorophenyl)difluorophosphorane ($(C_6F_5)_3PF_2$) using Janzen's route of oxidative fluorination of the triarylphosphine with XeF_2 again.[172,176] When the compound was obtained, subsequent fluoride abstraction reactions were attempted promptly. However, the compound was so electron-poor that even the addition of $B(C_6F_5)_3$ did not afford any phosphonium fluoride species, leaving the difluoride virtually untouched. Only the use of an even stronger acid in the form of $[Et_3Si]B(C_6F_5)_4$ allowed access to the desired phosphonium fluoride, $[(C_6F_5)_3PF]^+$. This highly electron-poor and fluorophilic species indeed showed extraordinary chemical capabilities.

It was possible to apply it as an organocatalyst together with $HSiEt_3$ in hydrodefluorination reactions of fluoroalkanes (note, breaking the strongest C–X single bond known!) with as little as 1 mol% catalyst loading at room temperature in the course of one hour with excellent yields (up to >95%). The catalytic cycle is depicted in Scheme 8.



Scheme 8: Catalytic cycle for the hydrodefluorination of fluoroalkanes by electrophilic phosphonium fluorides as proposed by Stephan and coworkers.

After this breakthrough discovery of an application of electrophilic phosphonium fluorides several follow-up publications appeared, describing for instance hydrogenation of olefins in 2012,[177] olefin isomerization and hydrosilylation catalysis in 2013,[178] metal-free phosphine oxide reductions in 2016[179] and more, thereby exploring and broadening the utility of new phosphonium species as organocatalysts and awaking organophosphorus fluorine chemistry from its slumber. There is, however, a noteworthy catch in the newly revived chemistry of phosphonium fluorides. When examining the methods used for the synthesis of the required difluorophosphoranes, one will notice that all of them rely on the application of expensive XeF_2 or worse, fluorine gas. The field thus suffers from the same limitations that we had previously tackled for the cases of RSF_5 and $RTeF_5$ discussed in chapters 2 and 3. With the knowledge for the oxidative fluorination of chalcogens in hand, we felt well equipped for a leap to group 15 and to give the TCICA/KF approach a shot at pentels.

4.3 Results and Discussion

4.3.1 Phosphorus and TCICA – Remarks

To tackle the limited accessibility of organophosphorus(V) fluorides we attempted to draw on the experience we had gathered addressing the mild and gas-free oxidative fluorination of organodisulfides, -diselenides, and -ditellurides and more to provide access to highly fluorinated organoheteroatom species of group 16 before. So far, the performance of the TCICA/KF approach had been satisfactory and we opted to apply it for the oxidative fluorination of various phosphines as well.

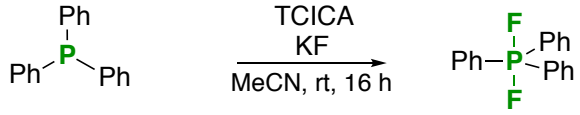
4.3.2 Phosphorus and TCICA – Screening

When considering starting materials to use in our screening, we opted for easy-to-handle, cheap and common PPh_3. An oxidative addition reaction to the phosphine would ideally result in PF_2Ph_3 as the product, which had previously been reported by Smith in 1960.[163] The initial thought was that oxidation of P(III) to P(V) was probably going to require similar, or fewer equivalents of TCICA than the oxidation of disulfides to RSF_4Cl compounds (S(I) to S(VI)). So, we performed the first reaction with 18 equiv. TCICA and 32 equiv. KF with 10 mol% TFA in MeCN at room temperature for 16 h. The outcome of the unoptimized reaction was promising. We obtained full conversion of the starting material (>99% ^{19}F NMR yield) and an isolated yield for the difluorinated PF_2Ph_3 of 42%. Using this encouraging first result as a starting point, we began screening to optimize our reaction conditions. Table 15 summarizes our findings.

As in the cases of all other heteroatom-substituted arenes before, the reactions were carried out in non-deuterated solvents and monitored by ^{19}F NMR and ^{31}P NMR spectroscopies. Due to much better resolution, yields given in Table 15 are ^{19}F NMR yields. Best yields of PF_2Ph_3 with the least amounts of reagents were obtained when 6 equiv. TCICA and 16 equiv. KF were used. Contrasting the results for the dichalcogenide substrates, the yield of the reaction does not profit from the addition of catalytic amounts of acid. Here, we again screened Lewis and Brønsted acids alike, neither of which resulted in an improved yield. On the contrary, the application of stoichiometric amounts of TFA frequently led to the formation of $OPPh_3$ instead, likely due to minor contaminations of the acid with moisture, resulting in hydrolysis of the putative P(V) species. Another difference to the oxidative fluorination of group 16 elements was found in the solvent screening. Even though MeCN produced the best results again, the use of EtOAc and acetone did indeed result in the formation of PF_2Ph_3, although in the former case with reduced yields. In the case of acetone, however, the yield was comparable to that obtained in acetonitrile and the choice for MeCN as the preferred solvent was simply made for the sake of practicality as obtaining and maintaining a stock of dry acetone proves to be significantly more challenging than for

the nitrile solvent. Performing the reaction in $MeNO_2$ did not yield any product. Surprisingly, NCS or NCPhth can be used as replacements for TCICA, but afforded significantly lower yields. In summary, it was determined that best ^{19}F NMR yields of >99% of PF_2Ph_3 can be obtained by stirring PPh_3 with 6 equiv. TCICA and 16 equiv. KF in MeCN overnight at room temperature.

Table 15: Screening for optimized conditions of the oxidative fluorination of PPh_3.

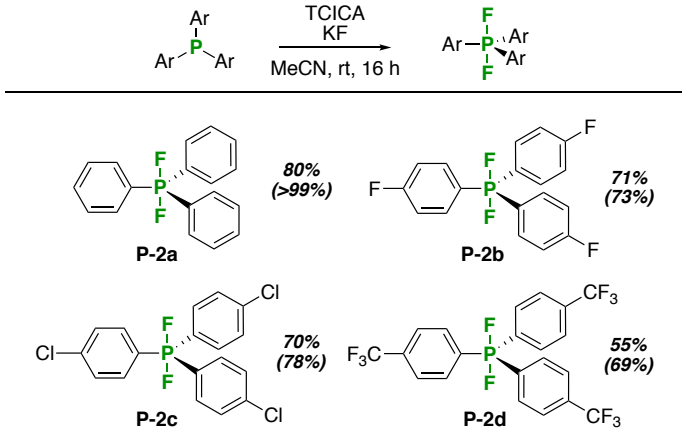


entry	*TCICA(equiv.)*	*KF (equiv.)*	*TFA (equiv.)*	*yield (%)*	*notes*
1	18	32	0.1	quant.	-
2	18	32	0	quant.	-
3	18	16	0	quant.	-
4	9.0	32	0	quant.	-
5	9.0	16	0	quant.	-
6	4.5	16	0	66%	-
7	2.0	16	0	58%	-
8	6.0	24	0	84%	-
9	**6.0**	**16**	**0**	**quant.**	**-**
10	5.0	16	0	90%	-
11	4.0	16	0	56%	-
12	3.0	16	0	50%	-
13	6.0	16	0	98%	2 x conc.
14	6.0	16	0	0%	$MeNO_2$
15	6.0	16	0	77%	EtOAc
16	**6.0**	**24**	**0**	**96%**	**acetone**
17	6.0*	24	0	68%	*NCS
18	6.0**	24	0	69%	**NCPhth
19	6.0***	24	0.1***	84%	***$ZnCl_2$

4.3.3 Phosphorus and TCICA – Scope

After completion of the screening procedure, we explored the substrate scope of the reaction, encountering its strengths along with the first limitations (Table 16). The procedure tolerates electron-withdrawing groups, such as halogens (**P-2b** and **P-2c**) and the trifluoromethyl substituent (**P-2d**) in meta- and para- positions well. Initial attempts using tris(2-fluorophenyl)phosphine and tris(pentafluorophenyl)phosphine as substrates resulted in unclear and complicated ^{19}F NMR spectra. Purification by extraction did not afford the clean PR_3F_2 species but a mixture of products (PR_3F_2, $K[PR_3F_3]$, and unidentified side products). As expected, the TCICA/KF method reaches its limits when extending the scope to mildly electron-donating groups or alkyl substituents. Phosphines with either class of substituents run into known background reactions with TCICA (e.g. ring chlorination, benzylic chlorination for electron-rich arenes and P–C bond cleavage for alkyl substituents).[101] This, congruent with our findings for chalcogenides, limits the scope of the TCICA/KF approach to relatively electron-deficient triarylphosphines. Isolation of the PR_3F_2 species can be achieved through filtration of the reaction mixture, subsequent solvent (MeCN) evaporation, extraction of the (solid) residue with n-hexane:DCM (10:1) followed by a second filtration, and finally solvent evaporation *in vacuo*. Unfortunately, isolation of the compounds following the described route requires various steps that have to be performed with meticulous exclusion of air and moisture as organophosphorus(V) fluorides tend to hydrolyze rapidly. The latter aspect frequently leads to the formation of triarylphosphine oxides as a side product of the reaction which are notorious for their difficult separation from other products. Although we were able to obtain pure, oxide-free PR_3F_2 compounds **P-2a**–**P-2d**, the problem was a persistent one and further limited the applicability of the TCICA/KF approach in the specific case of triarylphosphines. However, the compounds we had obtained were at large known from previous publications, thus we were able to confirm the NMR spectroscopic data collected therein and ^{19}F, as well as ^{31}P example spectra of such compounds, are shown below in subchapter 3.3.6. Following Muetterties' rule for the stereochemistry of trigonal bipyramidal compounds, the fluorine atoms, having the highest apicophilicity, assume the

Table 16: Scope of PR_3F_2 species accessed by application of the TCICA/KF approach to triarylphosphines.



Isolated yields. ^{19}F NMR yields in brackets.

axial positions in the bipyramidal structure.[165] Thus, out of the three thinkable isomers, i.e. zero, one or two fluorine atoms occupying the axial positions, only the latter is actually observed. The resulting structure exhibits D_{3h} symmetry, rendering both F atoms chemically and magnetically equivalent, which leads to a doublet in the ^{19}F NMR spectra. Correspondingly, the ^{31}P NMR spectrum shows coupling between the phosphorus central atom and both equivalent fluorine ligands resulting in a triplet. Detailed information about chemical shifts and coupling constants is, again, given in subchapter 3.3.6. As encouraging as the results we obtained with TCICA/KF in the cases of disulfides, ditellurides, and derivatives thereof were, the limitations in terms of purification and scope subjectively outweighed the practicality of the approach by the avoidance of XeF_2 in the synthesis of triaryldifluorophosphoranes.

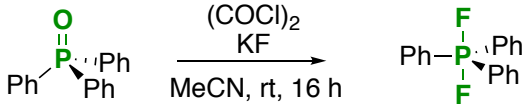
4.3.4 Oxalyl Chloride – Difluorophosphoranes and Salts thereof

With the limitations in mind, we looked for other routes that would i) not require oxidation of the phosphines and could thus allow for more electron-rich and alkyl-substituted substrates and ii) solve the problems that we encountered upon purification of the R_3PF_2 species, hopefully avoiding lengthy, multiple filtrations and thus formation of any oxides altogether. The inspiration for our solution ironically came from a paper by Stephen *et al.* that, for once, did not focus on phosphonium fluorides or difluorophosphoranes but instead applied organophosphorus(V) chlorides ($[R_3PCl]^+$ species) as intermediates for the reduction of tertiary phosphine oxides to tertiary phosphines.[180] The paper describes the synthesis of various $[R_3PCl]^+$ species by treatment of the corresponding OPR_3 with oxalyl chloride ($(COCl)_2$) in chloroform and subsequent reduction at 130°C under 80 bar H_2 pressure. This synthetic route to phosphonium chlorides is not new. It has first been described in 1977 by Masaki and Fukui who showed that $(COCl)_2$ is a very efficient desoxychlorination reagent for triorganylphosphines.[181] The reaction mechanism was recently analyzed in detail by DFT calculation carried out in the Grimme group in 2019.[182] Additionally, Schmutzler and coworkers had previously described the synthesis of similar phosphonium bromide compounds from tertiary phosphines with elemental bromine already in 1982 and were able to show that they can be used as precursors for the synthesis of difluorophosphoranes.[183] We thought that a combination of the procedures by Schmutzler and Fukui might solve both aforementioned problems as the starting materials would now be phosphine oxides (note: with phosphorus in the oxidation state +V), which do not require further oxidation and might therefore allow access to difluorophosphoranes with more sensitive organic substituents. Furthermore, by using oxides from the beginning, accidental formation of any P=O species would not be a problem throughout the reaction. Helpful in the choice of reaction conditions was a recent publication by the Gilheany group

who investigated the solution behavior of phosphonium chlorides in 2018.[184] The group had discovered a solvent dependent equilibrium between the phosphonium chloride ([R_3PCl]Cl) and the dichlorophosphorane (R_3PCl_2) species.

They were able to show that the phosphonium analogues are the major species in polar solvents like MeCN, chloroform or DCM (which likely stabilize the positive charge in these compounds) whereas less polar solvents like benzene, toluene and THF favor the uncharged dichlorophosphoranes in solution.

Table 17: Screening data for optimized conditions of the desoxygenative fluorination of $OPPh_3$.



entry	*$(COCl)_2$ (equiv.)*	*KF (equiv.)*	*yield (%)*	*notes*
1	18	32	quant.	-
2	18	32	quant.	-
3	9	32	quant.	-
4	9	16	quant.	-
5	9	16	quant.	-
6	4.5	16	quant.	-
7	3	16	quant.	-
8	3	8	91%	-
9	**3**	**12**	**quant.**	**-**
10	3	6	90%	-
11	2	12	82%	-
12	3	12	quant.	2 x conc.
13	3	12	quant.	40 °C
14	3	12	63%	toluene
15	3	12	0%[a]	DCM
16	3	12	77%	EtOAc
17	3	12	quant.[b]	acetone
18	3	12	98%[b]	2 x conc. in acetone
19	3	12	84%	0.1 equiv. TFA[c]
20	3	12	80%	0.1 equiv. $ZnCl_2$[c]
21	3*	12	38%	*$SOCl_2$ instead of $(COCl)_2$
22	3	12*	quant.	*CsF instead of KF
23	3	12*	48%	*CaF_2 instead of KF

a: only phosphonium chloride ^{31}P NMR and no fluorination visible
b: minor side products due to reaction between acetone and $(COCl)_2$
c: Additive

As we aimed for a Cl–F exchange following the desoxychlorination step, a free "coordination site" on phosphorus as found in the phosphonium species was thought to be beneficial to the reaction. Thus, we performed an initial reaction of triphenylphosphine oxide with 5 equiv. $(COCl)_2$ and 32 equiv. KF in MeCN at room temperature. Amazingly enough, the reaction resulted in the complete conversion of the starting material to triphenyldifluorophosphorane with an initial ^{19}F NMR yield of >99%.

With this incredibly promising finding at hand, we began screening for reaction conditions that would afford complete conversion but might allow us to save reagent equivalents in the process (Table 17).

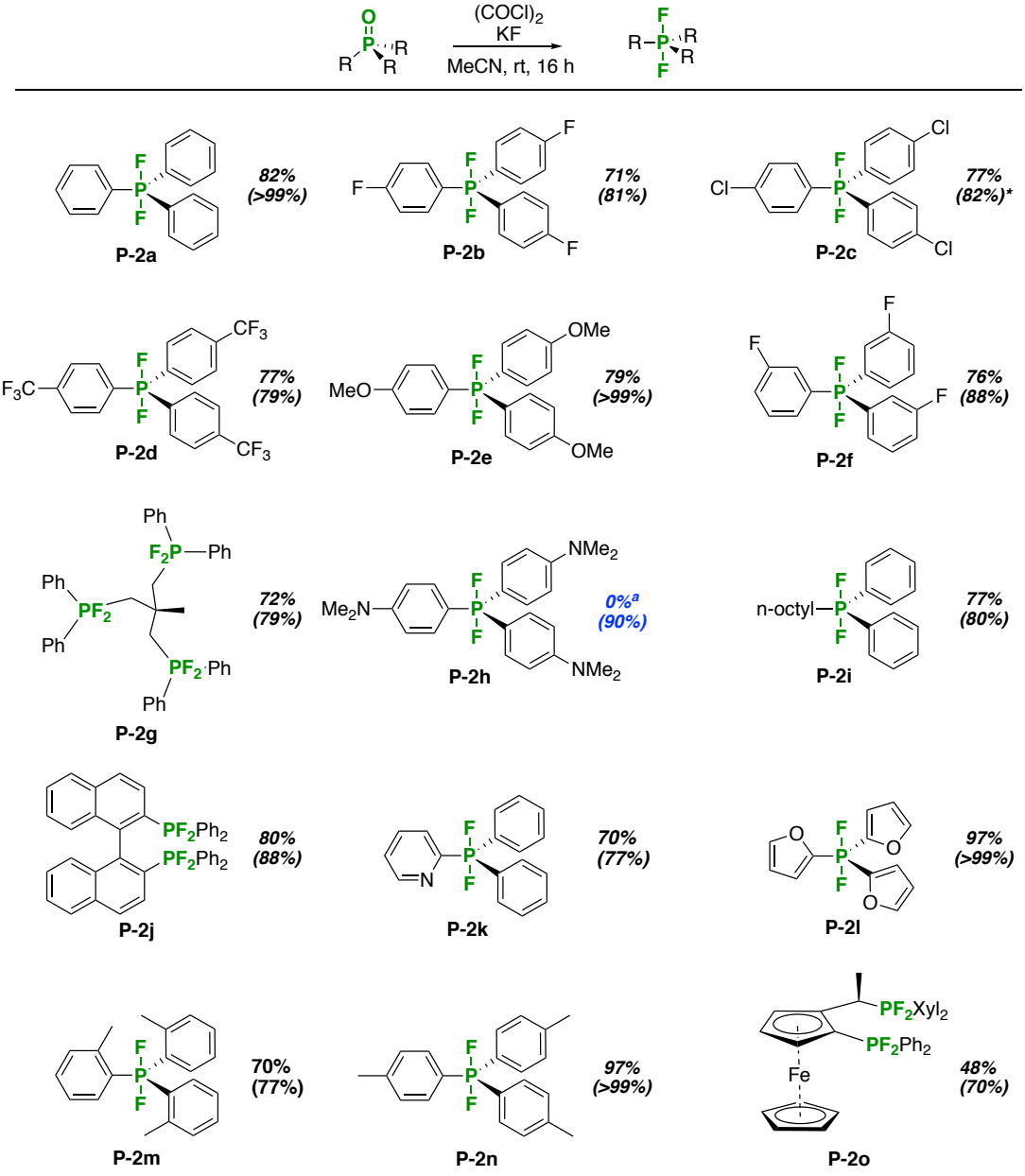
All reactions during screening were carried out in non-deuterated solvents, hence, the reported yields are ^{19}F NMR yields. Interpretation of the screening data revealed that best yields of PPh_3F_2 were obtained when 3 equiv. $(COCl)_2$ and 12 equiv. KF were used. For reactions (screening and scope) exclusively spray-dried KF was used to allow for the highest reproducibility. Contrary to the TCICA/KF approach it is not important for the applied fluoride sources (here KF), additives and solvents to be rigorously dried. Hydrolysis of PPh_3F_2 results in the re-formation of $OPPh_3$ which would undergo another desoxygenative chlorination cycle by reaction with $(COCl)_2$. However, it might be important to increase the amount of $(COCl)_2$ used in those cases. When screening for additives, we found that neither the addition of Brønsted nor Lewis acids allow for lower amounts of $(COCl)_2$ to be applied. The reaction is thus best performed without any additives. In solvent screening, best results were, analogous to the TCICA/KF method, obtained with MeCN. The use of DCM led to the formation of phosphonium chloride only, likely due to the limited solubility of KF in the solvent. Employment of toluene or EtOAc resulted in acceptable but lower yields than for MeCN. Interestingly, like in the case for the TCICA/KF oxidative fluorination of PPh_3, the reaction performs equally well in acetone. As rigorous drying is not necessary in this specific reaction, switching solvents for MeCN to acetone can be considered. However, we opted for MeCN as most studies focusing on this reaction and product type did not apply any acetone as the solvent and instead frequently revolved around MeCN or DCM. Finally, no significant side reactions occur when heating the reaction mixture to 40 °C.

Best results are thus obtained with 3 equiv. $(COCl)_2$, 6 equiv. KF in MeCN at room temperature overnight.

4.3.5 Oxalyl Chloride – Scope

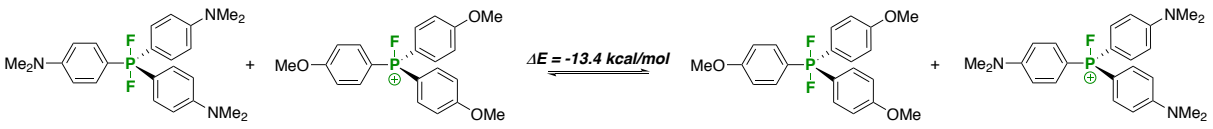
Having established the optimized reaction conditions for the desoxygenative fluorination of $OPPh_3$, we proceeded to explore the scope of the reaction for a wide variety of triorganylphosphine oxides. All oxides apart from $OPPh_3$, which was already available in our lab, were synthesized using a standard procedure involving the dissolution of the corresponding phosphine in DCM followed by addition of excess H_2O_2 and stirring of the reaction mixture overnight.[185] The organic and aqueous phases are separated and the organic phase is concentrated to afford the phosphine oxide which is then used without further purification.

Table 18: Scope of PR_3F_2 species accessed by application of the $(COCl)_2$/KF approach to triarylphosphine oxides.



Isolated yields. ^{19}F NMR yields in parantheses. [a]Exclusively the corresponding phosphonium fluoride is observed, isolated yield thereof given in parantheses.

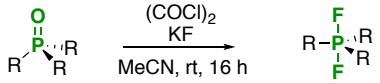
The optimized reaction conditions were applied to the phosphine oxide starting materials, allowing us to assess the utility and shortcomings of the newly developed $(COCl)_2$/KF approach (Table 18). Discussing the former first, we found that, congruent with the TCICA/KF approach, the procedure tolerates standard electron-withdrawing groups like halogens in **P-2b**–**P-2d** as well as a trifluoromethyl substituent in **P-2f**, in *meta*- and *para*-positions, well. In stark contrast to the TCICA/KF approach, however, is the discovery that the procedure also tolerates electron-donating substituents on the aryl group giving compounds **P-2e** or **P-2h** in excellent yields. Interestingly, the inclusion of multiple phosphine oxides as in compounds **P-2g** or **P-2j** does not pose any problems and both fluorinated species were obtained in very good yields. Furthermore, the procedure tolerates heteroaromatic compounds (**P-2k** and **P-2l**) as well as alkyl derivatives (**P-2i**). It was even possible to synthesize and characterize Xyliphos derivative **P-2m** by NMR although a conclusive ^{13}C NMR spectrum was not obtained as the species tends to decompose in solution over time, as indicated by a darkening of the initially bright orange solution. After the starting material was fully converted, the products are typically obtained in an extremely straightforward procedure involving filtration (to remove excess KF) followed by evaporation of the solvent and excess $(COCl)_2$ *in vacuo*. One of the most interesting findings in our exploration of PR_3F_2 chemistry concerns compound **P-2h**. As reported in Table 18, we did not obtain any difluorophosphorane in this case but rather the phosphine oxide was fully converted into its phosphonium fluoride counterpart. We were able to isolate the compound, fully characterize it and obtain a crystal structure (*vide infra*). We believe that the phosphonium species is too electron-rich to be subjected to a nucleophilic attack because of the very low σ_{para} constant for the dimethylamino group of -0.83, compared to a σ_{para}(OMe) value of -0.27. Changing the fluoride source to more soluble NMe_4F or CsF did not change the outcome of the reaction.[186] Furthermore, we performed a DFT calculation to find the energies of the isodesmic reaction shown in Scheme 9, which gave values consistent with the experimental data showing that formation of the phosphonium fluoride of **P-2h** is favored over the one of **P-2e** by 13.4 kcal/mol (DFT ωB97XD/6-311++G**).[187,188]

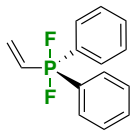


Scheme 9: Isodesmic reaction calculated with DFT (ωB97XD/6-311++G**) comparing NMe_2 vs. OMe substituent stabilizing effects.

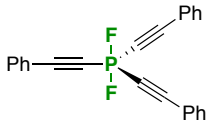
Aside from the obvious upsides of the $(COCl)_2$/KF when compared to either XeF_2 or TCICA/KF, there are of course limitations to the procedure (Table 19). Firstly, alkenyl substituted phosphine oxide **P-2n** as well as the alkynyl substituted variant **P-2r**, unfortunately, lead to the formation of various unidentified side products, presumably due to a reaction of the double-bond with oxalyl chloride or in a self-immolating process. Interestingly, alkynyl compound **P-2o** was formed without the occurrence of any side products. The reaction was, however, exceedingly slow so that even after 48 h only about 30% of the starting material was consumed and converted into the difluorophosphorane. A reason for this is probably found in the lowered electron density on phosphorus when comparing the alkynyl species to the aryl-substituted compounds (this will be further explored when discussing a putative mechanism in subchapter 3.3.8). When the reaction mixture is heated (50°C) to increase its rate, multiple side products are formed, again presumably from reaction of the C–C multiple bonds with $(COCl)_2$. In an attempt to prepare **P-2p** under the standard condition did not afford any conversion of the starting material, presumably due to the poor nucleophilicity of the oxygen ligand. When carbon-based substituents are replaced for nitrogen-based ones, as in compound **P-2q**, another limitation becomes apparent and P–N bond cleavage occurs and the corresponding diphenyltrifluorophosphorane (or diphenyltetrafluorophosphate, respectively) is obtained instead. Lastly, when all three purely carbon-based arenes are swapped for heteroarenes as in **P-2s**, the reaction produces several unidentified side products only. Those limitations made it impossible to isolate any of the compounds shown in Table 19.

Table 19: Limitations of the $(COCl)_2$/KF approach.

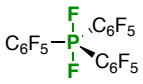




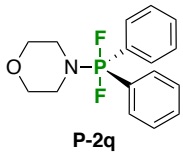
P-2n



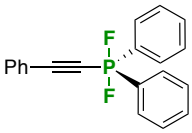
P-2o



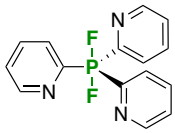
P-2p



P-2q



P-2r



P-2s

Difluorophosphoranes not isolated.

4.3.6 NMR Spectroscopic Details of R_3PF_2 species and Their Salts

The isolation of difluorophosphoranes given in Table 18 allowed us to fully characterize the compounds and assess their NMR spectroscopic properties. The general pattern for the compounds is very similar and chemical shifts with coupling constants are discussed using molecule **P-2l** as an example. As discussed before, ^{19}F NMR spectra of PR_3F_2 species typically show a doublet (unless a substituent also bears F atoms), corresponding to the two axial fluorine atoms. In the case of **P-2l** this signal appears at -64.37 ppm with a large $^{1}J(P-F)$ coupling constant of 675.1 Hz. Accordingly, the ^{31}P NMR shows a triplet at -89.9 Hz. The signals in both spectra are shown below (Figure 31).

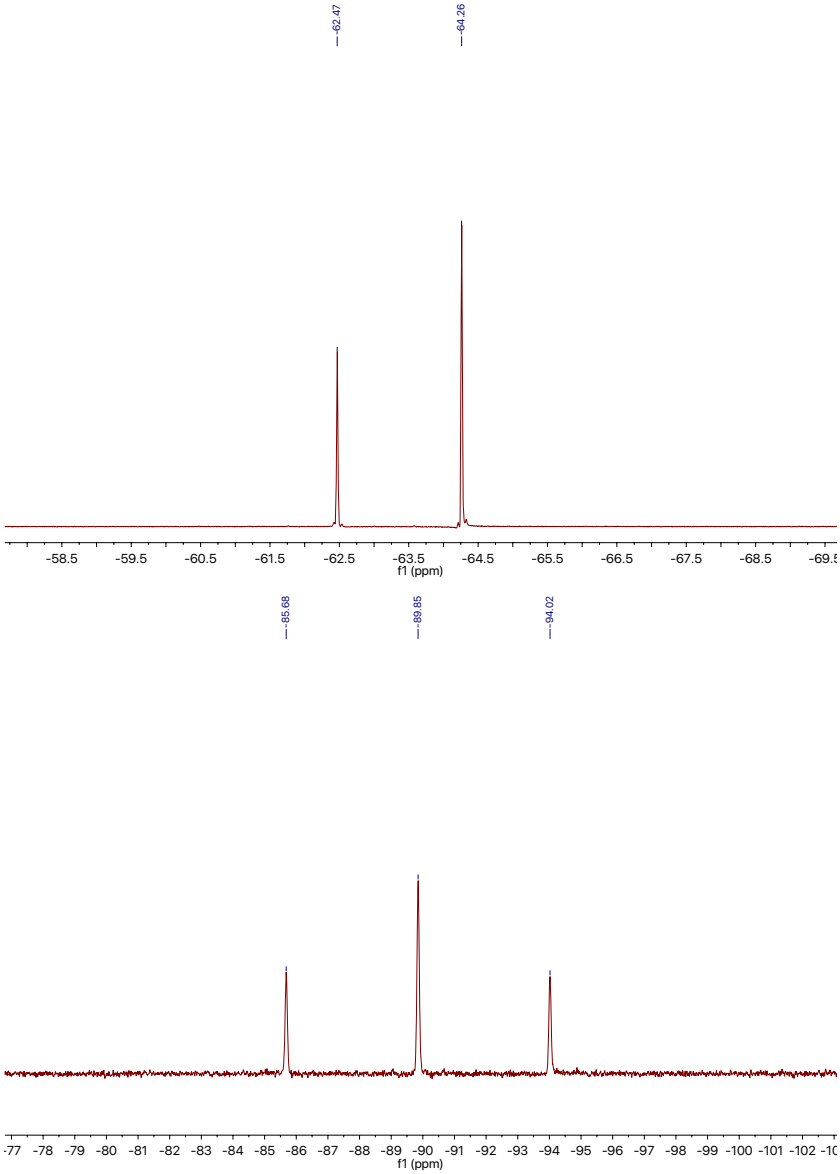


Figure 31: Typical ^{19}F NMR (top) and ^{31}P NMR (bottom) spectra of R_3PF_2 compounds in MeCN-d_3, as illustrated for **P-2l.**

As mentioned above, compound **P-2h** showed a deviating behavior from the rest of the difluorophosphoranes in that only the corresponding triarylphosphonium fluoride was formed with no detectable difluorination product. We nevertheless isolated the compound and characterized it in terms of its NMR spectroscopic properties (Figure 32). The ^{19}F NMR now reveals a doublet at -109.94 ppm with a very large $^{1}J(P\text{-}F)$ coupling constant of 971.93 Hz. The strong downfield shift in comparison to PR_3F_2 analogues is expected for a strongly deshielded cationic species. The ^{31}P NMR spectrum also varies drastically from the spectra of the difluoro counterparts. The single F atom leads to a doublet at 90.0 ppm instead of the triplet typically observed for difluorophosphoranes. The spectra are in good agreement with literature data for comparable phosphonium species like $[Ph_3PF][FB(C_6F_5)_3]$ (^{19}F NMR: δ (P–F) = -128.3 ppm, ^{1}J = 996 Hz and ^{31}P NMR: δ = 94.7 ppm).[189]

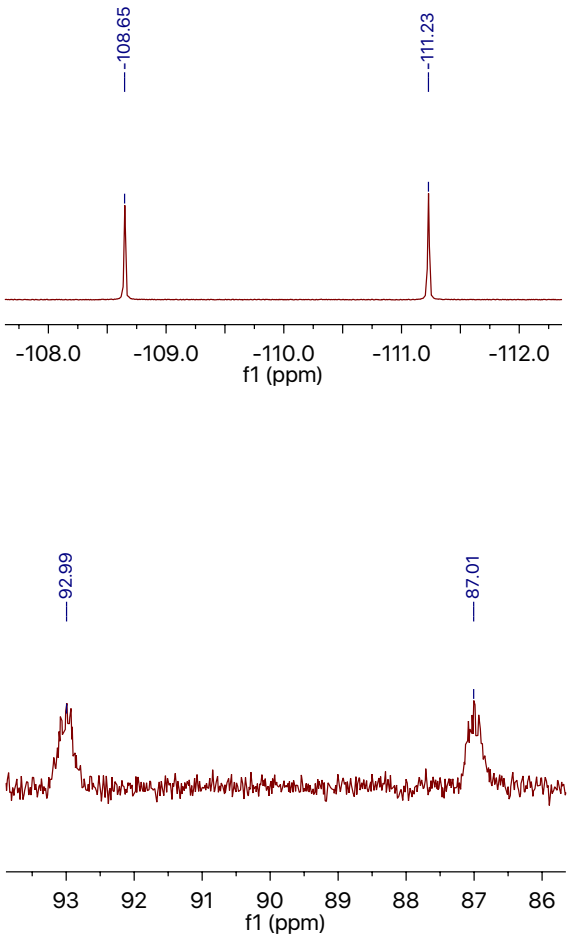


Figure 32: ^{19}F NMR (top) and ^{31}P NMR (bottom) spectra of **P-2h** in MeCN-d_3.

4.3.7 Solid State Analysis of R_3PF_2 species

Apart from the spectroscopic characterization, we were also able to successfully determine the crystal structures of the difluorophosphoranes **P-2c**, **P-2l** and **P-2g** with multiple PF_2-units, as well as phosphonium salt **P-2h**. Crystals of compound **P-2c** were obtained by slow evaporation of a solution of the compound in *n*-hexane:DCM (1:1). It crystallizes in the triclinic space group $P\bar{1}$ and shows the expected trigonal bipyramidal structure with the two fluorine atoms in the axial positions (Figure 33). Bond lengths of 1.6653(9) Å and 1.6725(9) Å were measured for the P–F bonds. The P–C bonds have an average bond length of 1.820 Å. Examination of the almost linear P–F bond angle of 177.25(5)° and the averaged angles θ(F–P–C) with 89.95° and θ(C–P–C) with exactly 120° revealed that the structure deviates only very slightly from the ideal trigonal bipyramidal geometry.

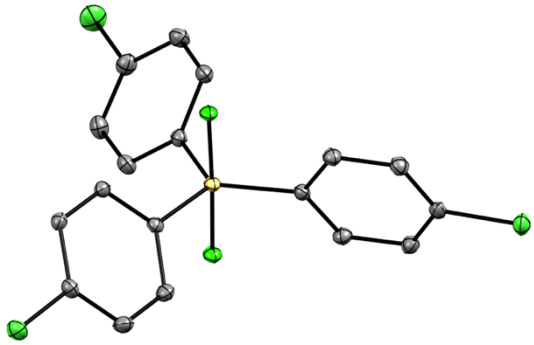


Figure 34: ORTEP view of **P-2c**. Hydrogen atoms omitted for clarity (displacement ellipsoids at 50% probability level).

Like for **P-2c**, crystals of **P-2l** were obtained by slow evaporation of a solution of the compound in *n*-hexane:DCM (1:1). It crystallizes in the monoclinic space group C2/c with two symmetry independent molecules within the asymmetric unit and, like **P-2c**, exhibits a slightly distorted trigonal bipyramidal geometry (Figure 34). The P–F bonds are 1.644(8) Å long, and thus in good agreement with the analogous bond lengths in **P-2c**. P–C bond lengths of 1.784(2) Å were found, also congruent with the respective bonds in **P-2c**. The F–P–F angle of 179.43(7)° only deviates slightly from linearity. The averaged angles θ(F–P–C) and θ(C–P–C) are 90.00° and 120.00°, respectively. Other than for the two previous difluorophosphoranes, crystals of **P-2g** were obtained by layering a solution in 1,2-difluorobenzene with *n*-hexane at room temperature (Figure 35). The compound crystallized in the cubic space group $Pa\bar{3}$.

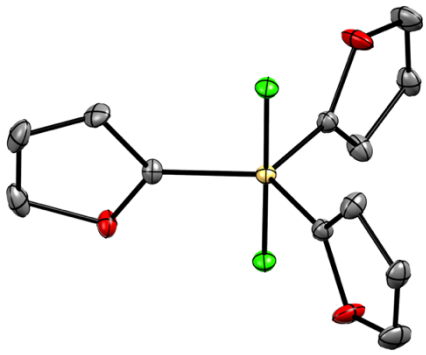


Figure 33: ORTEP view of **P-2l**. Hydrogen atoms omitted for clarity (displacement ellipsoids at 50% probability level).

The asymmetric unit contains one-third of a molecule, with the bond between the tertiary carbon and the methyl group aligned with a crystallographic 3-fold axis. This extraordinarily high symmetry leads to a near-ideal trigonal bipyramidal structure around the central phosphorus atoms with θ(F–P–F), θ(F–P–C) and θ(C–P–C) angles of 178.30(5)°, 90.00° and 120° respectively (the last two angles are averaged over the three PF_2-units). Concerning bond lengths, the compound is in excellent agreement with **P-2c** and **P-2l**. The P–F bonds have an average length of 1.679 Å whereas the P–Ph bonds are 1.825 Å long.

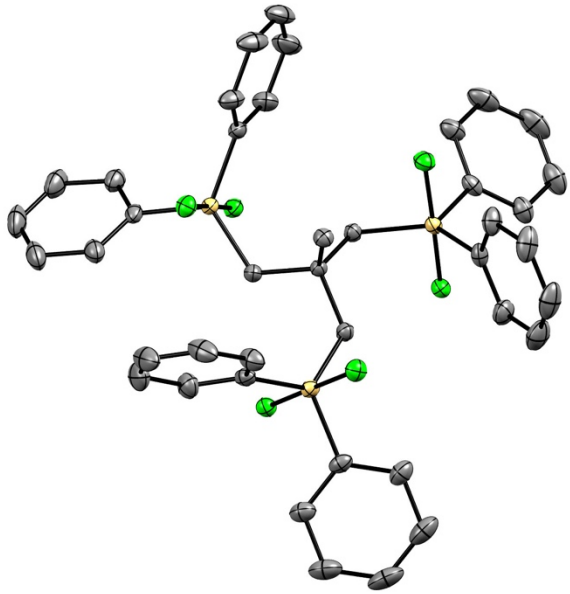


Figure 35: ORTEP view of **P-2g**. Hydrogen atoms omitted for clarity (displacement ellipsoids at 50% probability level).

Drastically different from the aforementioned difluorophosphoranes in terms of geometry is compound **P-2h** (cubic space group $Pa\bar{3}$). Due to its cationic, tetravalent nature, the compound assumes a distorted tetrahedral geometry (Figure 36). Unfortunately, the XRD data was of insufficient quality to allow for a detailed discussion of bond lengths and angles. However, the obtained data confirms the structure predicted by NMR spectroscopy of **P-2h** as, indeed, a cationic phosphonium fluoride.

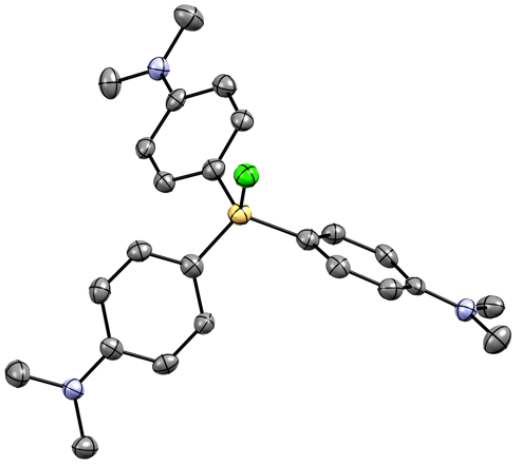
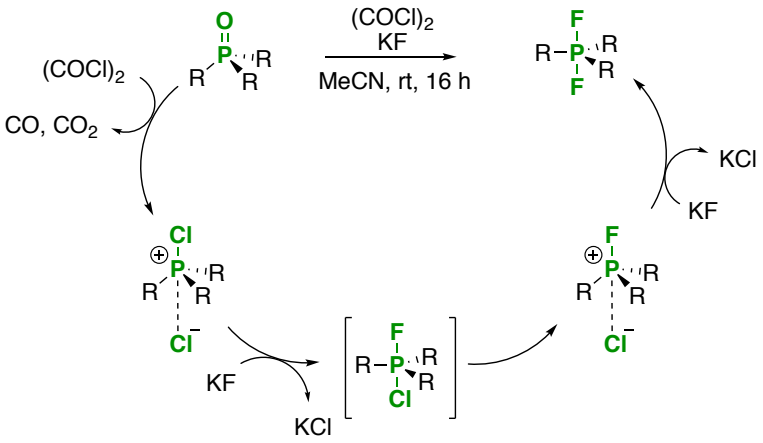


Figure 36: ORTEP view of **P-2h**. Hydrogen atoms and counteranions omitted for clarity (displacement ellipsoids at 50% probability level).

4.3.8 Mechanistic Considerations

The following section discusses hypotheses on the mechanism of the above-described desoxyfluorination of OPR_3 species by $(COCl)_2$/KF. It should be noted that no mechanistic experiments have been performed and the following considerations are of a purely theoretical nature and seem plausible considering the reaction conditions.

As depicted in Scheme 10 a reasonable first step for the reaction of OPR_3 with oxalyl chloride is the desoxychlorination that has been explored in detail by Masaki, Fukui and the Grimme groups before.[181,182] Occasionally, we were able to observe the formation of corresponding phosphonium chlorides *in situ* by ^{31}P NMR shortly after the addition of $(COCl)_2$ and thus confirm their previous findings. The resulting phosphonium chloride species presumably undergoes a nucleophilic attack by dissolved fluoride, resulting in a transient chlorofluorophosphorane, the only species in the proposed mechanism that we never observed. The latter experiences a dissociation of the less strongly bound chloride, forming a phosphonium fluoride in the process. This step seemed plausible as we were indeed able to isolate one of those phosphonium fluoride species in the case of **P-2h**. The final step is the association of the second fluoride, resulting in the formation of the difluorophosphorane.



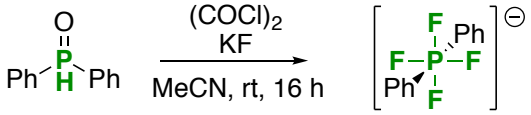
Scheme 10: Putative mechanism for the reaction of triorganylphosphine oxides with $(COCl)_2$/KF. Apart from the chlorofluorophosphorane on the bottom, all species were observed.

4.3.9 Trifluorophosphoranes and Salts thereof – Screening

Having successfully explored the scope of the new $(COCl)_2$/KF approach for difluorophosphoranes, we turned our attention to secondary phosphine oxides. Learning from the experience and conditions required in the synthesis of PR_3F_2 compounds, we applied similar conditions to diphenylphosphine oxide in an initial desoxyfluorination attempt. Fortunately, we found that treatment of the secondary phosphine with 18 equiv. $(COCl)_2$ and 32 equiv. KF in MeCN resulted in the formation of potassium tetrafluorodiphenyl phosphate, $K[Ph_2PF_4]$ in quantitative yield according to ^{19}F NMR spectroscopy after 16 h at room temperature. Interestingly, no trifluorophosphorane was detected. This can likely be attributed to the increased Lewis acidity and lower steric encumbrance of such trifluorinated species when compared to their difluoro-counterparts, which makes association of a fluoride more favorable. Encouraged by our initial result, we began screening for the optimal reaction conditions, this time screening only for reagent equivalents. As always, all reactions during screening were carried out in non-deuterated solvents, hence, the reported yields are ^{19}F NMR yields.

Our analyses of the acquired NMR data revealed that best yields of $K[Ph_2PF_4]$ were obtained when 3 equiv. $(COCl)_2$ and 8 equiv. KF were used (Table 20).

Table 20: Screening data for optimized conditions of the desoxygenative fluorination of diphenylphosphine oxide.



entry	*$(COCl)_2$ (equiv.)*	*KF (equiv.)*	*yield (%)[a]*	*notes*
1	18	32	quant.	-
2	18	32	quant.	-
3	9	32	quant.	-
4	9	16	quant.	-
5	9	16	quant.	-
6	4.5	16	quant.	-
7	3	16	quant.	-
8	3	12	quant.	-
9	**3**	**8**	**quant.**	**-**
10	3	6	81%	-
11	2	6	62%	-

a: yield corresponding to $K[PPh_2F_4]$

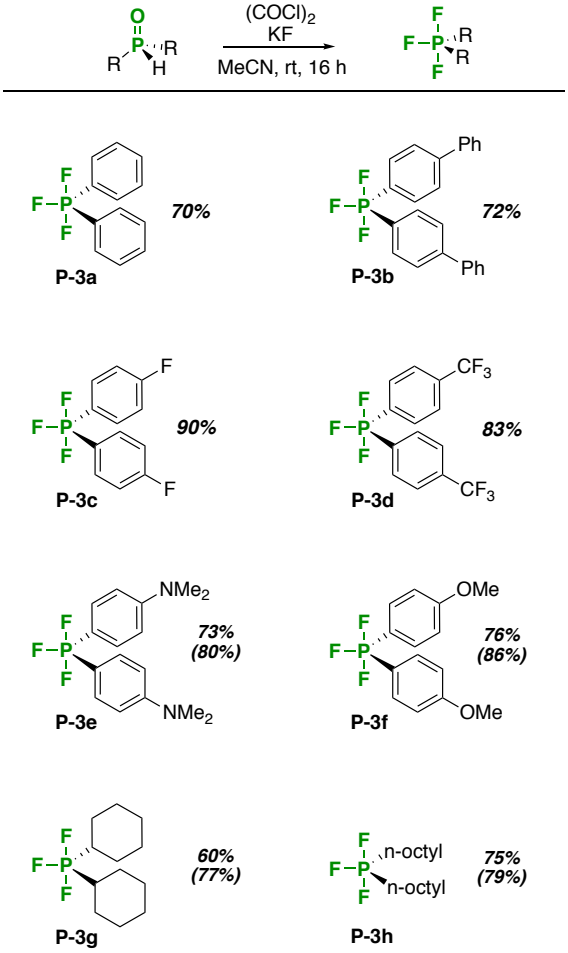
In analogy to the reactions carried out for PR_3F_2 species, exclusively spray-dried KF was used in all reactions (screening and scope) to allow for the highest reproducibility. Hydrolysis of $K[Ph_2PF_4]$ results in the formation of $OPPh_2F$, which reacts only very slowly under $(COCl)_2$/KF conditions and should thus be avoided. Our tests have shown that reacting $OPPh_2F$ under the reaction conditions only affords the desired $K[Ph_2PF_4]$ after 64 h. However, it is possible that heating of such hydrolyzed species under the reaction conditions could afford the desired products in good yields and relatively short reaction times even with "wet" fluoride sources, though this has not been tested.
In summary, best results are obtained with 3 equiv. $(COCl)_2$, 8 equiv. KF in MeCN at room temperature overnight.

4.3.10 Trifluorophosphoranes and Salts thereof – Scope

Having optimized the reaction conditions for the desoxyfluorination of secondary phosphine oxides, we started to explore the scope of our new approach with this substrate class (Table 21). All oxides apart from $OPHPh_2$, which is commercially available, were synthesized from $OPH(OEt)_2$ by treatment with organolithium or Grignard reagents under

known literature conditions.[190] In accordance with the substrate scope of PR_3F_2 compounds, we found that the reaction tolerates both electron-poor (**P-3a**–**P-3d**) and electron-rich (**P-3e**–**P-3f**) arene-substituted substrates alike. Also, in agreement with the difluoro analogues, the method tolerates well alkyl-substituted starting materials, as in **P-3g** and **P-3h**. However, we found that the outcome of the reaction and composition of the products is highly dependent on the nature of said starting materials. A closer examination revealed that, interestingly, choosing the appropriate substrate, the methodology allows access to both neutral or anionic fluorinated phosphorus(V) compounds. When analyzing the outcome of the reactions the following trends were observed. Substrates with aryl- or alkyl-based electron-rich substituents bound to the phosphorus atom provide R_2PF_3 compounds directly (**P-3e**–**P-3h**). If instead substrates with more withdrawing substituents bound to phosphorus are applied, conversion to $K[R_2PF_4]$ products – named **P-4a**–**P-4d** following the **P-3** series – is favored (*vide infra*). Again, preferential formation of fluorophosphates in the latter case is likely due to the enhanced Lewis acidity and lower steric encumbrance at the central atom in R_2PF_3 compared to R_3PF_2. Naturally, in the case of the octahedral fluorophosphates, two stereoisomers – the *cis*- and *trans*-forms – can be observed. The ratio in which these isomers forms. differs between substrates and we were not able to determine a clear trend favoring either one of the isomers. Unfortunately, their high moisture sensitivity made separation of the isomers hard to impossible. The ratios of *cis*- vs. *trans*-isomer for tetrafluorophosphates of the **P-4** series are listed in the experimental section (*vide infra*). Purification of compounds in the **P-3** series is dependent on the nature (neutral vs. ionic) of the product in question. For compounds **P-3e**–**P-3h** isolation is achieved in analogy to the difluorophosphoranes of the **P-2** series. Hence, the reaction mixture is filtered to remove excess KF and the solvent, together with excess $(COCl)_2$, is removed *in vacuo* to afford the pure trifluorophosphoranes. In case further impurities (typically in the

Table 21: Scope of PR_2F_3 species accessed by application of the $(COCl)_2$/KF approach to diorganylphosphine oxides.

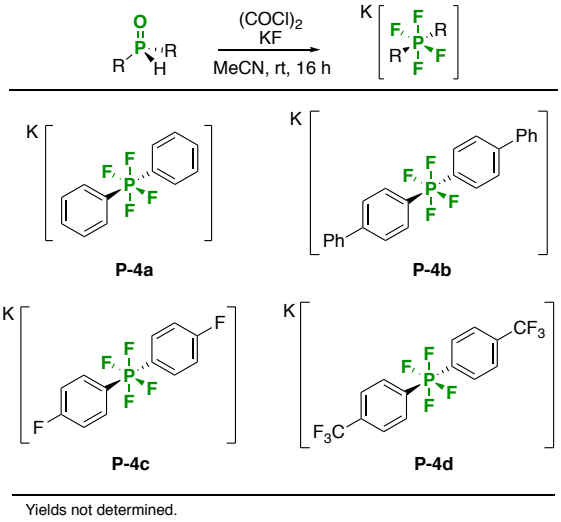


Isolated yields. ^{19}F NMR yields in parantheses.

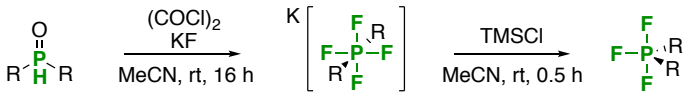
form of hydrolysis products) are present, the compounds can be extracted and/or recrystallized from DCM/hexane (1:10).

For ionic compounds **P-4a**–**P-4d** purification can be achieved by filtration, solvent removal under reduced pressure and subsequent washing of the solid residue, affording pure fluorophosphates. In the course of this research, our focus was, however, not on the synthesis of such anionic species and so no yields were determined. The four tetrafluorophosphates species synthesized in the course of this work are listed in Table 22.

Table 22: Scope of PR_2F_3 species accessed by application of the $(COCl)_2$/KF approach to diorganylphosphine oxides.



Yields not determined.



Scheme 11: General route to $[R_2PF_4]^-$ and R_2PF_3 species using $(COCl)_2$/KF and TMSCl in a two-step procedure.

Interestingly, it was possible to convert tetrafluorophosphates **P-4a**–**P4-d** to their trifluorophosphorane counterparts following a straightforward procedure and the resulting neutral trifluorophosphorane equivalents **P-3a**–**P-3d** were subsequently investigated in detail. Synthesis of the trifluorophosphoranes can be achieved by treatment of the **P-4** phosphate salts with TMSCl in anhydrous MeCN at room temperature (Scheme 11).

The reaction results in the instantaneous formation of TMSF, a volatile compound easily removed *in vacuo*, as well as KCl, indicated by formation of a colorless precipitate. Accordingly, the products are purified by filtration (removing KCl) and subsequent solvent removal under reduced pressure, which afforded **P-3a**–**P-3d** in excellent yields (see Table **P-3a**–**P-3d**).

4.3.11 NMR Spectroscopic Details of R_2PF_3 species and Their Salts

Having successfully isolated the compounds in Tables 21 and 22, we went on to analyze them by NMR spectroscopy. Following the rules for apicophilicity discussed previously, one would expect two sets of chemically (and magnetically) inequivalent fluorine atoms within the R_2PF_3 species, with two fluorine atoms assuming the apical positions and the third F atom residing in an equatorial position of the trigonal bipyramid. As a result, the ^{19}F spectra should show two different sets of signals with the apical F atoms coupling to the central P atom and the unique F atom, resulting in a doublet of doublets (dd), integrating

to two F atoms. Additionally, the equatorial F atom couples to its apical counterparts and the P atom, leading to a doublet of triplets (dt) with an integral of one. Accordingly, the ^{31}P NMR spectrum should show a dt for the central P atom, as the apical P-F bonds are expected to be longer, resulting in a smaller coupling constant. Indeed, these patterns could be observed for all species in Table 21. As an example, the spectra of **P-3f** are shown in Figure 37. The ^{19}F NMR spectrum shows the two sets of signals at -38.76 ppm (^{1}J(P-F) = 823.61 and ^{2}J(F-F) = 35.89 Hz) and 78.70 ppm (^{1}J(P-F) = 953.64 and ^{2}J(F-F) = 35.89 Hz), whereas the ^{31}P NMR spectrum shows the expected dt at -36.8 ppm.

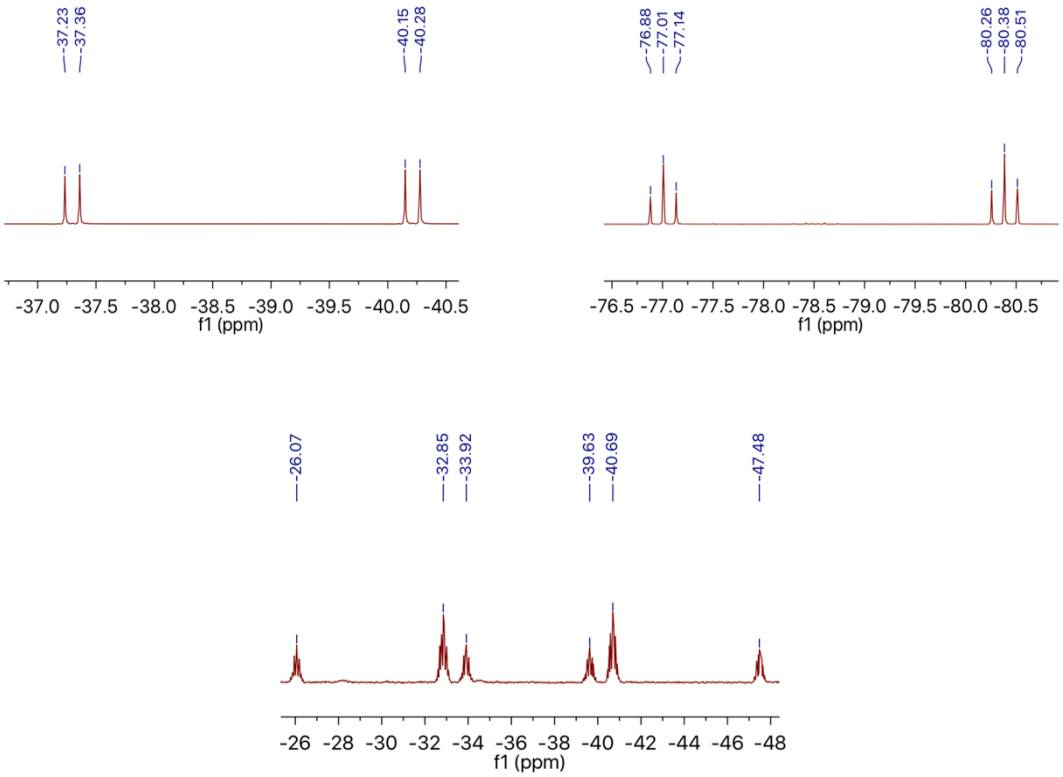


Figure 37: Typical ^{19}F NMR (top) and ^{31}P NMR (bottom) spectra of R_2PF_3 compounds in MeCN-d_3, as illustrated for **P-3f**.

NMR spectra for tetrafluorophosphates of the **P-4** series were more complicated than those of their **P-3** counterparts. In all cases, mixtures of the two conceivable isomers (*cis* and *trans*) were obtained. Luckily, however, their signals did not overlap in the ^{19}F NMR spectra, allowing us to determine their ratios by simple integration. While the *trans*-isomers show a single doublet in the ^{19}F NMR spectrum due to ^{1}J coupling between the central P atom and the magnetically equivalent fluoro ligands, the *cis*-isomer shows two sets of doublets of triplets, corresponding to the two sets of magnetically inequivalent fluorine atoms that couple to the central P atom as well as to each other. Tetrafluorophosphate **P-4b** serves as an example (see Figure 38).

The ^{19}F NMR spectrum shows the doublet for *trans*-**P-4b** at -45.04 ppm (^{1}J(P-F) = 871.2 Hz) as well as the two doublets of triplets for *cis*-**P-4b** at -41.48 ppm (^{1}J(P-F) = 719.9 Hz, ^{2}J(F-F) = 36.8 Hz) and -67.62 ppm (^{1}J(P-F) = 783.3 Hz, ^{2}J(F-F) = 36.8 Hz). The ^{31}P NMR spectrum shows the strongly overlapping pentet and triplet of triplets of both isomers around -120 ppm to -150 ppm.

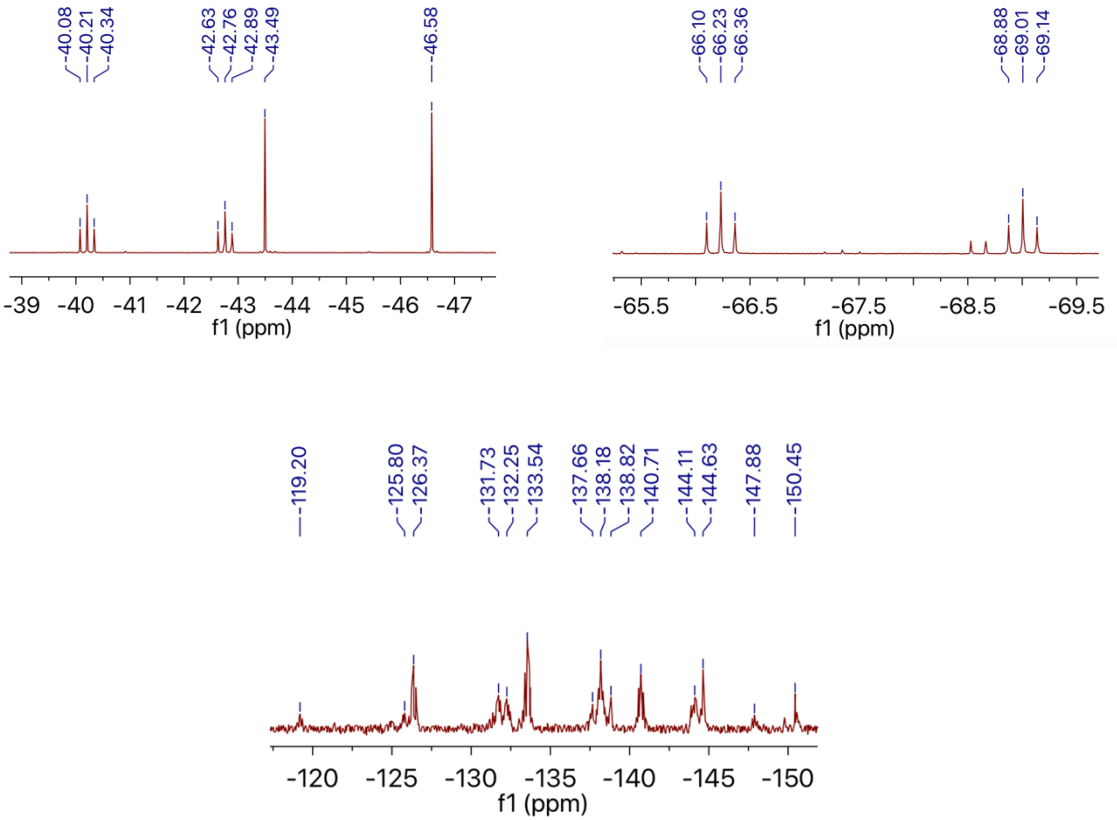


Figure 38: Typical ^{19}F NMR (top) and ^{31}P NMR (bottom) spectra of K[R_2PF_4] compounds in MeCN-d_3, as illustrated for cis- and trans-**P-4b**.

4.3.12 Solid State Analysis of Tetrafluorophosphate P-4b

Unfortunately, we were not able to obtain crystals suitable for X-ray diffraction for a trifluorophosphorane. However, tetrafluorophosphate *cis*-**P-4b** did afford crystals suitable for XRD measurements by slow evaporation of a saturated solution of **P-4b** and KF in MeCN (Figure 39). The compound crystallizes in the triclinic space group $P\bar{1}$ and the asymmetric unit contains four symmetry-independent moieties, with half a co-crystallized acetonitrile solvent molecule per moiety.

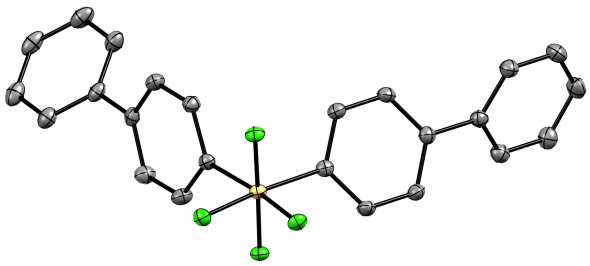


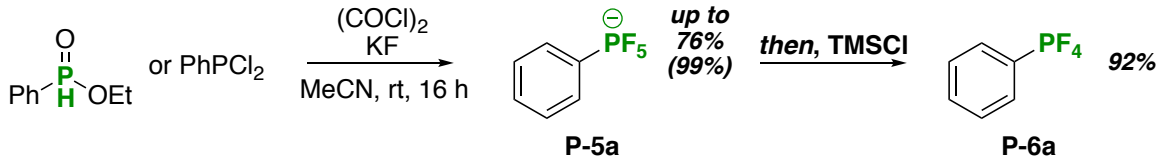
Figure 39: ORTEP view of cis-**P-4b**. Hydrogen atoms and counteranions omitted for clarity (displacement ellipsoids at 50% probability level).

The bond lengths are similar to those in the previously described difluorophosphoranes. The P–F_{eq} bond, are on average 1.685 (1.671(1)-1.694(1)) Å long, whereas the P–Fax bonds show an average length of 1.639 (1.632(1)-1.662(1)) Å. As expected the P–C bonds are significantly longer with an average of 1.851 (1.842(2)-1.857(2)) Å. In terms of shape, the anion has a nearly ideal octahedral structure with average θ(F_{ax}–P–F_{ax}), θ(F_{ax}–P–F_{eq}), θ(F_{ax}–P–C), θ(F_{eq}–P–C_{trans}) and θ(C–P–C) angles of 171.9°, 87.1°, 93.0°, 173.3° and 96.7°.

4.3.13 Oxalyl Chloride – Application to Further Phosphorus-, Arsenic- and Antimony-based Oxides

Apart from the two extensive scopes for di- and trifluorophosphoranes discussed above, we also explored the accessibility of various other group 15 substrates, based on phosphorus, arsenic and antimony. Although those studies were not as detailed, their results are briefly discussed below for the sake of completeness.

Firstly, tetrafluorophosphorane **P-6a** can be accessed by application of the oxalyl chloride/KF approach on ethyl phenylphosphinate. Similarly, to the trifluorophosphoranes, **P-6a** cannot be accessed directly but is instead obtained from its fluoride adduct **P-5a** by treatment of the latter with TMSCl in MeCN (Scheme 12).

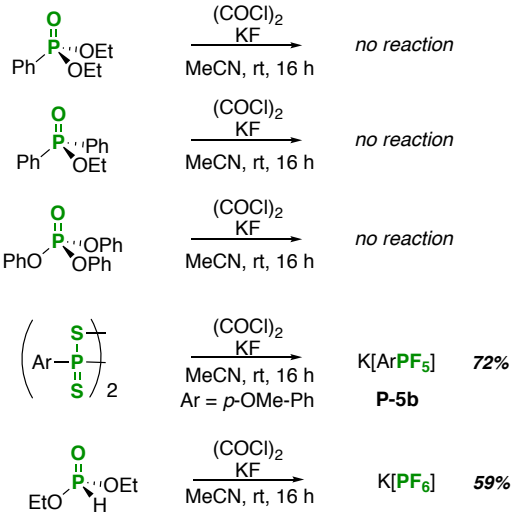


Scheme 12: Route to **P-5a** and **P-6a** species using $(COCl)_2$/KF and TMSCl in a two-step procedure.

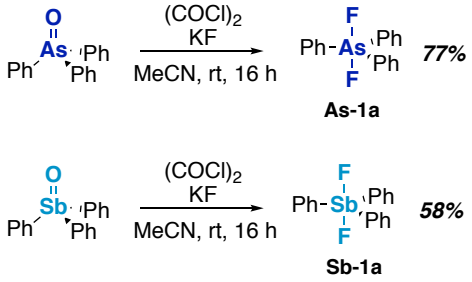
We also found that, instead of ethyl phenylphosphinate, $PhPCl_2$ can be used as a convenient starting material to afford **P-5a** and **P-6a** (in 76% and 92% yield, respectively). As addressed in the limitations section above, we had already found that N–P bonds are labile under the standard reaction conditions, having now discovered that O–P bonds behave similarly, we briefly explored the lability of various heteroatom–P bonds under our desoxygenative fluorination conditions. Interestingly, this study showed that P–OR bonds are converted to P–F bonds only under certain conditions in combination with hydride or amino substituents at the phosphorus center. For example, the P–OR bonds stay intact when ethyl phenylphosphinate is replaced with diethyl phenylphosphinate or triphenyl phosphate. Furthermore, the desoxygenative fluorination reaction shuts down entirely. A similar trend was noted for diphenylphosphine oxide derivatives: When instead of diphenylphosphine oxide (**P-2a**), ethyl diphenylphosphinate is used, no reaction occurs. The behavior of P–S and P=S bonds under fluorination conditions was also studied using Lawesson's reagent; we found that all phosphorus-sulfur bonds are readily cleaved to provide

pentafluorophosphate **P-5b** in 72% yield. Application of the standard conditions to diethyl phosphite resulted in cleavage of both P–O bonds and thus formation of KPF_6 in 59% ^{19}F NMR yield (Scheme 13).

Finally, we became interested in the reactivity of other pnictogen oxides and tested how triphenylarsine oxide and triphenylstibine oxide reacted under the $(COCl)_2$/KF conditions (Scheme 14). In analogy to triphenylphosphine oxide, both compounds undergo desoxygenative fluorination and form **As-1a** and **Sb-1a** in 58% and 77% yields, respectively. Unlike their phosphorus congeners, difluorotriaryl-λ^5-stibanes may be subjected to purification via column chromatography and have found applications as precursors to pentavalent organoantimony compounds in main-group element chemistry.[191–194] As a consequence of harsh starting materials (AsF_3) and reagents (IF_5, HF, etc.), difluorotriaryl-λ^5-arsanes are less explored but have demonstrated some potential applications as fluorinating reagents.[195] Although further investigations in this direction are needed, these initial results serve as a proof-of-concept that oxalyl chloride/KF-based desoxygenative fluorination can translate beyond phosphorus in group 15 elements.



Scheme 13: Reactivity of other group 15 P-based substrates.



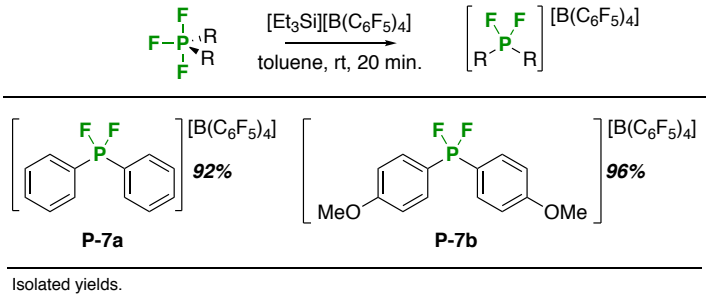
Scheme 14: Reactivity of As- and Sb-based substrates.

4.3.14 Diarylphosphonium Fluorides

After we explored the synthetic accessibility of different classes of P(V) fluorides and the development of the oxalyl chloride/KF procedure, we became interested in the applicability of the synthesized phosphoranes in catalysis. As previously discussed, Stephan and coworkers have described a variety of synthetic transformation catalyzed by phosphonium fluorides in earlier works, such as C-F bond functionalization,[174,176,196] carbonyl activation,[196,197] hydrosilylation,[196,198] CO_2 sequestration[174] and olefin hydrogenation[199]. Therein, the majority of the used organocatalysts were of the $[R_3PF]^+$ type. In their publications, they describe the synthesis of such organocatalysts mainly through defluorination of the corresponding difluorophosphoranes (R_3PF_2) by a silylium cation, usually $[SiEt_3{\cdot}(toluene)][B(C_6F_5)_4]$.

Inspired by their promising results we wanted to explore the usefulness of our approach for the synthesis of precursors to hitherto barely explored difluorophosphonium ($[R_2PF_2]^+$) cations. Thus, using **P-3a** and **P-3f** as electroneutral and electron-rich trifluorophosphorane substrates, we applied the literature conditions for the synthesis of $[R_3PF]^+$ species in an attempt to obtain the corresponding difluoro-phosphonium derivatives. Thus, **P-3a** and **P-3f** were dissolved in toluene and added to a stirred suspension of $[SiEt_3{\cdot}(toluene)][B(C_6F_5)_4]$ in toluene (Table 23). An immediate color change was indicative of an occurring reaction and after stirring for about 20-60 min., the reaction was left to settle and formed two layers. The bottom layer contained the desired phosphonium fluorides **P-7a** and **P-7b**, was separated from the top layer and washed with toluene and *n*-hexane to afford the salts in 92% and 96% yields as off-white spongy solids. We analyzed

Table 23: Scope of PR_2F_2 species accessed by application of silylium cations to difluorodiorganylphosphoranes.



Isolated yields.

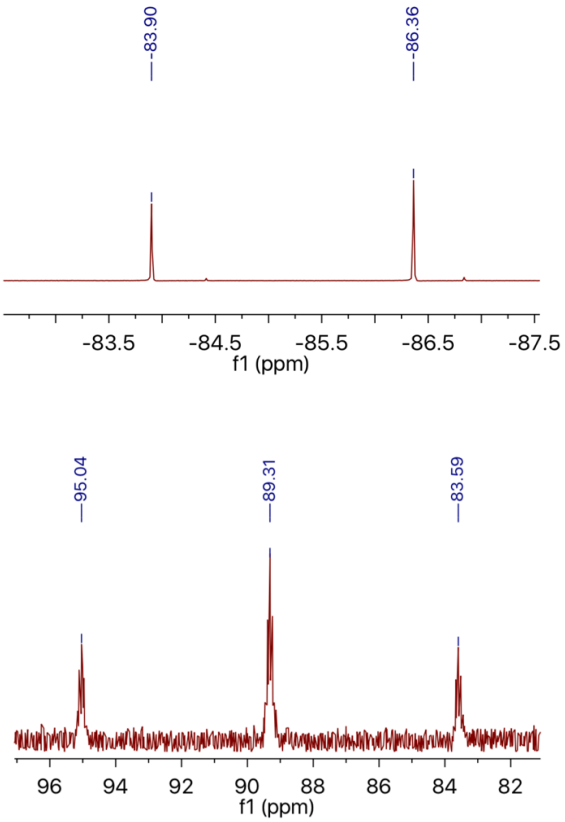


Figure 40: Typical ^{19}F NMR (top) and ^{31}P NMR (bottom) spectra of $[R_2PF_2]^+$ compounds in DCM-d_2, as illustrated for **P-7a**.

both compounds thoroughly by means of NMR spectroscopy, example spectra are shown in Figure 40.

As expected, the ^{19}F NMR spectrum shows a doublet for the two equivalent fluorine atoms at -85.13 ppm with a very large $^{1}J(P\text{-}F)$ coupling constant of 1159 Hz. Remarkably, this constant is even larger than the one observed for Stephans $(C_6F_5)_3PF^+$ organocatalyst, indicating very short P–F bonds and a high Lewis-acidity. The ^{31}P NMR spectrum revealed the complementary signals strongly shifted downfield, with a triplet at 89.31 ppm. With the two phosphonium species in hand, we set out to evaluate their viability as organocatalysts in defluorination reactions in analogy to Stephan's results. Thus, we dissolved the salts in DCM and treated the solution with $SiEt_3H$ and 1-fluorododecane, hoping to form dodecane (and $SiEt_3F$) in the process. Unfortunately, conversion occurred only to an unsatisfactory degree of less than 20%, which corresponded to the "catalyst" loading and indicates a stoichiometric conversion of 1-fluorododecane by the phosphonium species, rather than any catalytic reactivity. The results were comparable for **P-7a** and **P-7b** and were not improved by heating to 50°C. However, it was possible to show that the oxalyl chloride/KF approach is a viable tool for the synthesis of precursors to synthetically useful phosphonium species and further exploration in the direction of difluorophosphonium salts is necessary to evaluate their applicability as organocatalyst conclusively.

4.4 Conclusion

Novel strategies for the synthesis of fluorinated organophosphorus(V) compounds have been developed. For one, the oxidative fluorination of triorganylphosphines by easy-to-handle TCICA and KF was explored and applied to a handful of substrates. More interestingly, a straightforward method for the desoxygenative fluorination of phosphine oxides and other organophosphorus species, by application of oxalyl chloride and KF, was developed, its limitations were explored, and multiple extensive substrates scopes were produced. These simple conditions enable direct access to various compounds of the compositions R_3PF_2, R_2PF_3, $[R_2PF_4]^-$, $[R_2PF_2]^+$ $[R_3PF]^+$, $[RPF_5]^-$, RPF_4, PF_6^-, R_3AsF_2, as well as R_3SbF_2. All compounds were characterized by NMR spectroscopy and crystal structure analyses for multiple compounds were obtained. A simple strategy for the defluorination of fluorophosphates by application of TMSCl was developed and allowed access to a broader scope of fluorophosphoranes. The newly obtained R_2PF_3 compounds were used for the synthesis of the strongly underexplored compound class of difluorophosphonium ions using isolable $[SiEt_3{\cdot}(toluene)]^+$ silylium ions. Finally, these new $[R_2PF_2]^+$ compounds were subsequently investigated for their capability to function as Lewis-acid organocatalysts in the defluorination of 1-fluorododecane.

Chapter 5

General Conclusion and Outlook

5.1 General Conclusions

This doctoral thesis is focused on a frequently encountered problem in inorganic fluorine chemistry – accessibility. A key objective within this work was, hence, the development of safe, simple, and versatile approaches for the oxidative fluorination of heteroatom-bearing molecules.
To that end, two distinct methodologies have been investigated and applied to various main group elements.

The first method focused on the oxidative fluorination of diaryl dichalcogenides with the common swimming-pool disinfectant TCICA and KF as the fluoride source, allowing us to expand the scope of known SF_5- and TeF_5-substituted organic molecules in the process and to study the compounds in detail.
In the case of SF_5, this method opens a new pathway to aryl-SF_4Cl species – key intermediates to the highly sought-after pentafluorosulfanyl derivatives – without the necessity of typically required, difficult-to-handle reagents such as F_2, XeF_2, HF, SF_4 or Cl_2. At the same time, the method allows access to aryl-TeF_5 compounds, a largely unexplored substance class, in an equally straightforward, one-step procedure and thus helped us to extend the scope of known TeF_5 derivatives. Analysis of these molecules contributed to the fundamental understanding of the structure and bonding in these highly-interesting fluorides and facilitated an in-depth structural comparison between the SF_5 and TeF_5 groups as well as an evaluation of the reactivity of the latter under a variety of conditions.

The separately developed second method described in this thesis enables the desoxyfluorination of phosphane oxides by treatment with oxalyl chloride and KF. Similar to the previous method it allows for the synthesis of fluorinated heteroatom-bearing molecules without application of any hazardous fluorination agents like the ones mentioned above. Specifically, the method enabled the generation of a library of fluorophosphoranes and a detailed (NMR) spectroscopic analysis of the obtained species, thus eliminating an important synthetic barrier to further contributions in the field of phosphorus fluorine chemistry.

5.2 Personal Evaluation and Outlook

Even though the two methods developed throughout this doctoral thesis allow for a much more facile access to otherwise difficult-to-synthesize compounds, they are certainly not the Holy Grail of inorganic fluorine chemistry. Both still suffer from in-part severe and hardly understood, method-specific drawbacks, including limited functional group tolerance, by-product formation, the requirement of rigorously dried equipment and more, thus partially limiting the "user-friendliness" of the approaches presented herein. Furthermore, profound mechanistic insight into the TCICA method has barely been obtained. In hindsight this could have greatly helped to understand the fundamental limitations of the method, potentially allowing for adjustments and improvements of the methodology. Moreover, the applications of the oxalyl chloride method are, at this point in time, very specific to phosphorus-bearing molecules and have yet to be tested on other main group elements.

Thus, a lot of work is left for future inorganic fluorine chemists. The field is certainly vast, utterly underexplored and still lacks the clear fundamental experimental procedures that are characteristic for organic chemistry. All combined, those are facts that might intimidate and discourage a future generation of doctoral students from pursuing their studies in this area. To those chemists of the future, I would like to give a piece of advice. Although inorganic chemistry can be unforgivable, the field has much to offer, arguably much more than the typically well-defined, carbon-based chemistry that the vast majority of students pursue within their doctoral studies. Try looking at the periodic table as a chemical playground and don't only focus on the tedious sides of chemistry. Don't always pursue the most promising projects, as they frequently turn out to be the most predictable and dull ones. Do what a child would do on this playground. Explore, have fun and enjoy playing with your (pretty expensive) toys.

Chapter 6

Experimental

6.1 General Information

Unless otherwise stated, all reactions were carried out using a glove box or Schlenk technique under strictly anhydrous conditions and Ar or N_2 atmosphere. All solvents were either dried over molecular sieves or distilled using standard methods. Glassware was dried by heating at 160 °C for in an oven overnight or dried using a heat gun for several minutes under high vacuum. Commercially available chemicals were used without prior drying or purification. Spray-dried (or otherwise rigorously dried) KF was always weighed out under N_2 atmosphere in a glove box. Column chromatography was performed using a CombiFlash Rf200 system from Teledyne-Isco. All ^{1}H, ^{13}C, ^{19}F, ^{31}P and ^{125}Te NMR spectra were acquired on Bruker Avance 200, 300, 400, or 500 MHz spectrometers. For ^{19}F NMR yield determination, α,α,α-trifluorotoluene, fluorobenzene, or $NaPF_6$ was introduced after each reaction as an internal standard, and the d1 relaxation delay was increased to 10 s during data collection. The NMR chemical shifts are given in parts per million (δ) and calibrated to either residual solvent signal (^{1}H and ^{13}C), referenced indirectly via the ^{2}H signal of the lock substance (only ^{31}P NMR) or the internal standard. NMR data are reported in the following format: chemical shift (integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet (and combination of the above), coupling constants (Hz)). IR data was collected on a Thermo Fischer Scientific Nicolet 6700 FT-IR equipped with a PIKE technologies GladiATR or a Perkin-Elmer BX II using ATR FT-IR technology and absorption maxima are reported in cm^{-1}. GC/MS was performed on a Thermo Fischer Trace GC 2000 equipped with a flame ionization detector, using a ZB-5 column with guardian (L: 30 m, i.d.: 0.25 mm, DF = 0.25 μm) and helium as the carrier gas with a constant flow of 1.1 mL min–1 and a Shimadzu-QP 2010 Ultra using HP-5 column with a parallel MS and FID detection. HRMS data were collected by MoBiAS - the MS-service of the "Laboratorium für Organische Chemie der ETH Zürich" - or by the MS-service at the University of Zürich. Melting points (MP) were measured on the calibrated B-540 instrument by Büchi.Single crystalline samples were measured on a Rigaku Oxford Diffraction XtaLAB Synergy-S Dualflex kappa diffractometer equipped with a Dectris Pilatus 300 HPAD detector and using microfocus sealed tube Cu- or Mo-Kα radiation with mirror optics and a Bruker APEX-II fixed-chi diffractometer with sealed tube, graphite-monochromated Mo-Kα radiation. All measurements were carried out at 100 K using a cryostat. If necessary, samples were retrieved, prepared and mounted on Kapton micromounts (MiTeGen) under a nitrogen atmosphere at low temperatures (253 to 273K) using a μCHILL microscopy stage to prevent crystal damage by hydrolysis. Data collected on the Bruker instrument were integrated using SAINT from the Bruker Apex-II program. Data collected on the Rigaku instrument were integrated using CrysAlisPro and corrected for absorption effects using a combination of empirical (ABSPACK) and

numerical corrections.[200] The structures were solved using SHELXS[201] or SHELXT[202] and refined by full-matrix least-squares analysis (SHELXL)[201,203] using the program package OLEX2.[204] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters.

6.2 Experimental Details to Chapter 2

6.2.1 Procedures for Syntheses of Disulfide Starting Materials

The syntheses of diaryl disulfides were achieved following literature procedures.[95,97,205–208] Apart from novel molecules **S-1q** and **S-1x** the known disulfides were not thoroughly analyzed and so their characterization data is not reported herein as they had been accessed and characterized by other groups before. Their purity was confirmed by ^{1}H NMR. Disulfide starting materials for the synthesis of **S-2a**, **-2c**, **-2e**, **-2g**, **-2l**, **-2t**, **-2w**, **-2z**, **S-2aa** and **S-2ab** as well as **-3a** and **-3b** are commercially available, were bought and used as received.

General Procedure A for the Starting Materials of S-2b, **-2d**, **-2f**, **-2h**, **-2i**, **-2j**, **S-2k**, **S-2s** and **S-2y**.[206]

A substituted thiophenol substrate (10 mmol, 1.0 equiv.) was dissolved in 30 mL 1:5 H_2O:MeCN in a round-bottom flask equipped with a stir bar open to atmosphere. Iodine (5.0 mmol, 1.3 g, 0.5 equiv.) was added, and the reaction mixture was left to stir at room temperature for ca. 2 h. Afterwards reaction mixture was quenched with 30 mL 1% aqueous sodium thiosulfate and extracted into DCM. The combined organic layers were dried with Na_2SO_4, decanted, and concentrated in vacuo to provide pure disulfide. The compounds were not fully characterized as they've been accessed before.

General Procedure B for the Starting Materials of Compounds S-2n–2-p[207]

To a solution of the carboxylic acid-substituted disulfide substrate (10 mmol, 1.0 equiv.) in 50 mL DCM in a round-bottom flask under Ar atmosphere was added the corresponding alcohol (22 mmol, 2.2 equiv.), DCC (4.1 g, 20 mmol, 2.0 equiv.), and DMAP (0.26 g, 2.1 mmol, 0.2 equiv.). The reaction mixture was stirred at room temperature for 20 h. The precipitates were removed by filtration through Celite, and the filtrate was concentrated in vacuo. The crude material was purified via gradient column chromatography on silica gel, eluting with n-hexane:EtOAc, to provide the corresponding disulfide ester starting materials. The compounds were not characterized as they've been accessed before.

Procedure for Starting Material of Compound S-2r[205]

To a 50 mL Schlenk tube equipped with a stir bar was added potassium *tert*-butoxide (2.2 g, 20 mmol, 20 equiv.), thiourea (0.76 g, 10 mmol, 10 equiv.), and (4-bromo)benzophenone (0.26 g, 1.0 mmol, 1.0 equiv.). The tube was evacuated and refilled with Ar multiple times, then dried DMSO (20 mL) was added. The reaction mixture was stirred and irradiated with a UV pen lamp (302 nm) for 3 h, after which the reaction mixture turned dark brown. A mixture of iodine (0.26 g, 1.0 mmol, 1.0 equiv.) and potassium iodide (0.50 g, 3.0 mmol, 3.0

equiv.) was added, and the mixture was stirred until the dark brown color had faded. Water (30 mL) and conc. HCl (0.3 mL) were added, and the reaction mixture was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with H_2O, dried with $MgSO_4$, concentrated in vacuo, and purified via gradient column chromatography on silica gel, eluting with n-hexane:EtOAc, to provide the disulfide product as a light yellow solid in 72% yield (0.16 g, 0.36 mmol). The compound was not characterized as it has been accessed before.

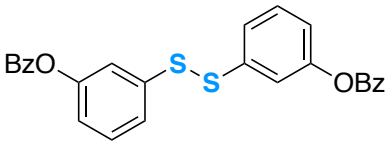
General Procedure C for Starting Materials of Compounds S-2u and S-2v[97]

2,5-dichloropyrimidine or 5-bromo-2-chloro-pyrimidine (10 mmol, 1.0 equiv.) was dissolved in 20 mL EtOH in a round-bottom flask equipped with a stir bar under Ar atmosphere, and the mixture was stirred. Thiourea (1.5 g, 20 mmol, 2.0 equiv.) was added, and the reaction mixture was heated to reflux for 18 h. Aqueous NaOH (1.1 g in 20 mL H_2O) was added, and the mixture was heated to reflux for an additional 2 h. Subsequently, the EtOH was removed using a stream of N_2. Upon addition of 2 mL 1 M HCl, the thiol intermediate precipitated from the solution as a bright yellow solid. The solid was recovered by filtration, washed with H_2O (3 x 10 mL), added to a new round-bottom flask equipped with a stir bar, and suspended in 30 mL H_2O. To the suspension was added NaOH (0.5 g), and the mixture was stirred at room temperature for 30 min. Subsequently, $K_3[Fe(CN)_6]$ (4.0 g, 12 mmol) was added, and the reaction mixture stirred at room temperature for 22 h. The resulting solid was recovered by filtration, redissolved in 20 mL DCM, dried with $MgSO_4$, filtered through Celite, and concentrated in vacuo to afford the disulfide products. These were carried forward without further purification. The compounds were not characterized as they've been accessed before.

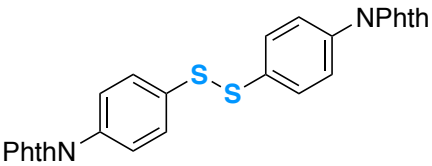
Procedure for Starting Material of Compound S-2m[209]

To a round-bottom flask equipped with a stir bar under Ar atmosphere was added 4,4'-disulfanediyldiphenol (4.0 g, 16 mmol, 1.0 equiv.), 50 mL THF, and 5 mL triethylamine; the mixture was stirred and cooled to 0 °C. Acetyl chloride (2.75 g, 35 mmol, 2.2 equiv.) was added dropwise via syringe. The reaction mixture was stirred and warmed to room temperature gradually over 2 h, then stirred for 16 h. A white precipitate was removed via filtration and washed with THF (3 x 5 mL). The resulting pale-yellow filtrate was concentrated in vacuo and dissolved in DCM. The organic layer was washed with sat. aqueous Na_2CO_3 (3 x 20 mL), washed with brine (1 x 10 mL), dried with $MgSO_4$, filtered through Celite, and concentrated in vacuo to provide the disulfide product as a white solid in 71% yield (3.8 g, 11 mmol). The compound was not characterized as it has been accessed before.

6.2.2 Specific Procedures and Analytical Data for Novel Disulfides



Disulfanediylbis(3,1-phenylene) dibenzoate (S-1q). To a round-bottom flask equipped with a stir bar under Ar atmosphere was added 3,3'- disulfanediyldiphenol (4.0 g, 16 mmol, 1.0 equiv.), 50 mL THF, and 5 mL triethylamine; the mixture was stirred and cooled to 0 °C. Benzoyl chloride (4.9 g, 35 mmol, 2.2 equiv.) was added dropwise via syringe. The reaction mixture was stirred and warmed to room temperature gradually over 2 h, then stirred for 16 h. A white precipitate was removed via filtration and washed with THF (3 x 5 mL). The resulting pale-yellow filtrate was concentrated in vacuo and dissolved in DCM. The organic layer was washed with sat. aqueous Na_2CO_3 (3 x 20 mL), washed with brine (1 x 10 mL), dried with $MgSO_4$, filtered through Celite, and concentrated in vacuo to provide the disulfide product as a viscous, pale-yellow oil in 82% yield (6.0 g, 13 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): 7.98-7.91 (5H, m), 7.46-7.35 (3H, m), 7.31-7.11 (8H, m), 6.91 (2H, d, J = 7.9 Hz); ^{13}C NMR (76 MHz, $CDCl_3$): 171.6, 164.6, 162.1, 151.2, 138.0, 134.3, 133.5, 130.3, 130.0, 129.8, 129.0, 128.7, 128.4, 128.2, 124.5, 120.6, 120.5. ν_{max} (ATR-IR): 1731 cm^{-1}. HRMS (ESI-TOF): calc'd for $C_{26}H_{22}NO_4S_2$ $[M+NH_4]^+$: 476.0985, found: 476.0988.



2,2'-(Disulfanediylbis(4,1-phenylene))bis(isoindoline-1,3-dione) (S-1x).[208] Phthalic anhydride (2.0 g, 14 mmol, 2.1 equiv.) was dissolved in glacial acetic acid (10 mL) in a round-bottom flask equipped with a stir bar under Ar atmosphere. Subsequently, 4,4'-disulfanediyldianiline (1.6 g, 6.5 mmol, 1.0 equiv.) in glacial acetic acid (5 mL) was added dropwise while stirring the solution. The reaction mixture was heated to reflux and stirred for 18 h. It was then quenched by pouring it into ice water (30 mL). The mixture was filtered, and the precipitate was washed with cold water (3 x 5 mL), washed with cold EtOH (3 x 5 mL), and dried in vacuo to afford the starting material for compound **S-2x** in 64% yield (2.11 g, 4.2 mmol) as a light brown solid; m.p. not determined (decomposes above 240 °C). ^{1}H NMR (300 MHz, $CDCl_3$): 7.96 (4H, dd, J = 5.2, 3.0 Hz), 7.80 (4H, dd, J = 5.2, 3.0 Hz), 7.65 (4H, d, J = 8.4 Hz), 7.44 (4H, d, J = 8.4 Hz); ^{13}C NMR (76 MHz, $CDCl_3$):

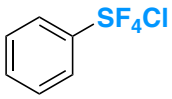
167.0, 136.7, 134.5, 131.7, 130.9, 127.9, 127.0, 123.8. ν_{max} (ATR-IR): 1705 cm^{-1}. HRMS (ESI-TOF): calc'd for $C_{28}H_{17}N_2O_4S_2$ $[M+H]^+$: 509.0624, found: 509.0632.

6.2.3 Procedure for the Synthesis of Aryl-SF_4Cl Compounds

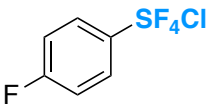
General Procedure D for the reaction of Disulfides with TCICA/KF

Trichloroisocyanuric acid (0.958 g, 4.1 mmol, 18 equiv.) was added to an oven-dried microwave vial equipped with a stir bar; the vessel was then transported inside a glove box under N_2 atmosphere. Spray-dried potassium fluoride (0.425 g, 7.3 mmol, 32 equiv.) was added to the reaction vessel, which was then sealed with a cap with septum using a crimper. The closed vial was removed from the glove box. Under Ar atmosphere, a solution of the disulfide/diselenide substrate (0.23 mmol, 1.0 equiv.) in 1.5 mL MeCN was added to the vial, followed by a solution of trifluoroacetic acid (1.8 μL, 0.02 mmol, 0.1 equiv.) in 0.5 mL MeCN. The reaction mixture was stirred vigorously at room temperature overnight (ca. 18 h). Subsequently, the crude reaction mixture was filtered into a PFA vessel via syringe filter and concentrated in vacuo. The crude reaction mixture was diluted with dry 9:1 *n*-hexane:DCM, filtered into another PFA vessel, and concentrated in vacuo. (*Note that repeating dilution and filtration multiple times prior to concentration may provide better yields.*) The obtained crude material consisted of mostly the aryl-SF_4Cl product and was carried forward without further purification.

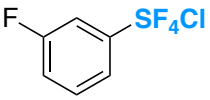
6.2.4 Analytical Data of Aryl-SF_4Cl Compounds



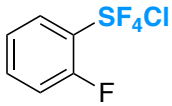
Chlorotetrafluoro(phenyl)-λ⁶-sulfane (S-2a). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[95] ^{19}F NMR (377 MHz, CD_3CN): +136.61 (4F, s).



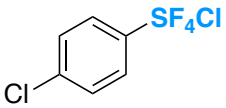
Chlorotetrafluoro(4-fluorophenyl)-λ⁶-sulfane (S-2b). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[95] ^{19}F NMR (377 MHz, CD_3CN): +137.65 (4F, s), -108.21 (1F, m).



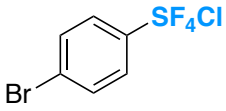
Chlorotetrafluoro(3-fluorophenyl)-λ⁶-sulfane (S-2c). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[210] ^{19}F NMR (282 MHz, CD_3CN): +136.08 (4F, s), -111.34 (1F, m).



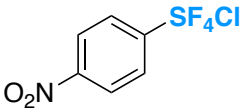
Chlorotetrafluoro(2-fluorophenyl)-λ⁶-sulfane (S-2d). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[95] ^{19}F NMR (282 MHz, CD_3CN): +140.30 (4F, d, J = 24.5 Hz), -110.04 (1F, m).



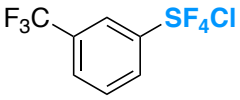
Chlorotetrafluoro(4-chlorophenyl)-λ⁶-sulfane (S-2e). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[95] ^{19}F NMR (282 MHz, CD_3CN): +136.75 (4F, s).



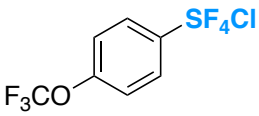
Chlorotetrafluoro(4-bromophenyl)-λ⁶-sulfane (S-2f). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[95] ^{19}F NMR (282 MHz, CD_3CN): +136.59 (4F, s).



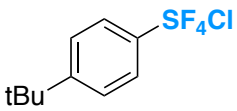
Chlorotetrafluoro(4-nitrophenyl)-λ⁶-sulfane (S-2g). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[95] ^{19}F NMR (377 MHz, CD_3CN): +135.02 (4F, s).



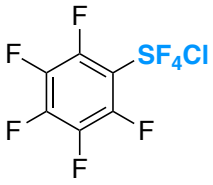
Chlorotetrafluoro(3-(trifluoromethyl)phenyl)-λ⁶-sulfane (S-2h). The reaction was run according to the **general procedure D**. ^{19}F NMR (377 MHz, CD_3CN): +135.61 (4F, s), -63.21 (3F, s).



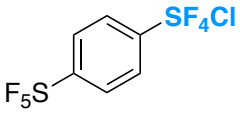
Chlorotetrafluoro(4-(trifluoromethoxy)phenyl)-λ⁶-sulfane (S-2i). The reaction was run according to the **general procedure D**, and the product was converted to the more stable, but volatile, pentafluorosulfanyl arene **S-4g**. ^{19}F NMR (282 MHz, CD_3CN): +136.73 (4F, s), -58.56 (3F, s).



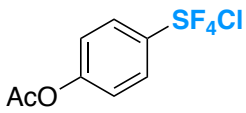
Chlorotetrafluoro(4-(tert-butyl)phenyl)-λ⁶-sulfane (S-2j). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[95] ^{19}F NMR (282 MHz, CD_3CN): +137.64 (4F, s).



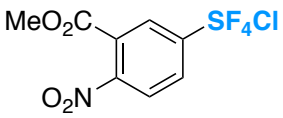
Chlorotetrafluoro(perfluorophenyl)-λ⁶-sulfane (S-2k). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[95] ^{19}F NMR (282 MHz, CD_3CN): *trans*- isomer: +143.21 (4F, t, J = 27.6 Hz), -135.35 (2F, m), -148.85 (1F, m), -161.05 (2F, m); *cis*-isomer: +153.07 (1F, q, J = 158.3 Hz), +122.77 (2F, ddd, J = 158.3, 95.1, 78.2 Hz), +79.21 (1F, dtt, J = 158.3, 95.1, 20.9 Hz), -135.35 (2F, m), -148.85 (1F, m), -161.05 (2F, m). *trans*:*cis* ratio: 1.5:1.



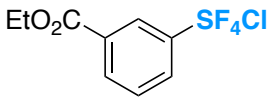
1-(Chlorotetrafluoro-λ⁶-sulfaneyl)-4-(pentafluoro-λ⁶-sulfaneyl)benzene (S-2l). The reaction was run according to the **general procedure D**, and the product was partially converted to the more stable, but volatile, 1,4-dipentafluorosulfanylbenzene for characterization. Note that conversion to 1,4-dipentafluorosulfanylbenzene was confirmed by GC/MS analysis (m/z = 329.9); yield n.d. ^{19}F NMR (377 MHz, CD_3CN): +134.96 (4F, s), +81.54 (1F, quint, J = 148.5 Hz), +61.86 (4F, d, J = 148.5 Hz).



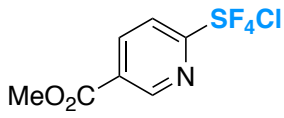
4-(Chlorotetrafluoro-λ⁶-sulfaneyl)phenyl acetate (S-2m). The reaction was run according to the **general procedure D**, and the product was converted to the more stable pentafluorosulfanyl arene **S-4a** to obtain complete characterization data. ^{19}F NMR (282 MHz, CD_3CN): +137.43 (4F, s).



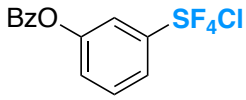
Methyl 5-(chlorotetrafluoro-λ⁶-sulfaneyl)-2-nitrobenzoate (S-2n). The reaction was run according to the **general procedure D**, and the product was converted to the more stable aryl tetrafluoro-λ⁶-sulfanyl alkene **S-5b** to obtain complete characterization data. ^{19}F NMR (282 MHz, CD_3CN): +134.63 (4F, s).



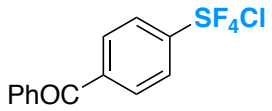
Ethyl 3-(chlorotetrafluoro-λ⁶-sulfaneyl)benzoate (S-2o). The reaction was run according to the **general procedure D**, and the product was converted to the more stable pentafluorosulfanyl arene **S-4c** to obtain complete characterization data. ^{19}F NMR (282 MHz, CD_3CN): +135.95 (4F, s).



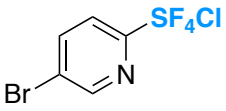
Methyl 6-(chlorotetrafluoro-λ⁶-sulfaneyl)nicotinate (S-2p). The reaction was run according to the **general procedure D**, and the product was converted to the more stable aryl tetrafluoro-λ⁶-sulfanyl alkane **S-5a** to obtain complete characterization data. ^{19}F NMR (282 MHz, CD_3CN): +123.52 (4F, s).



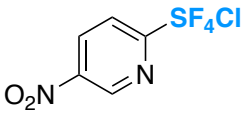
3-(Chlorotetrafluoro-λ⁶-sulfaneyl)phenyl benzoate (S-2q). The reaction was run according to the **general procedure D**, and the product was converted to the more stable pentafluorosulfanyl arene **S-4d** to obtain complete characterization data. ^{19}F NMR (282 MHz, CD_3CN): +136.39 (4F, s).



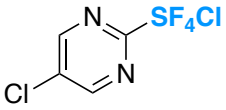
(4-(Chlorotetrafluoro-λ⁶-sulfaneyl)phenyl)(phenyl)methanone (S-2r). The reaction was run according to the **general procedure D**, and the product was converted to the more stable pentafluorosulfanyl arene **S-4h** to obtain complete characterization data. ^{19}F NMR (282 MHz, CD_3CN): +135.78.



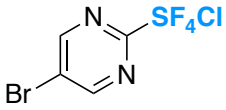
5-Bromo-2-(chlorotetrafluoro-λ⁶-sulfaneyl)pyridine (S-2s). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[210] ^{19}F NMR (282 MHz, CD_3CN): +124.66 (4F, s).



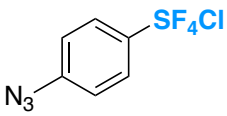
2-(Chlorotetrafluoro-λ⁶-sulfaneyl)-5-nitropyridine (S-2t). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[210] ^{19}F NMR (282 MHz, CD_3CN): +123.42 (4F, s).



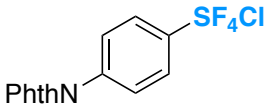
5-Chloro-2-(chlorotetrafluoro-λ⁶-sulfaneyl)pyrimidine (S-2u). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[210] ^{19}F NMR (282 MHz, CD_3CN): +119.06 (4F, s).



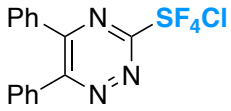
5-Bromo-2-(chlorotetrafluoro-λ⁶-sulfaneyl)pyrimidine (S-2v). The reaction was run according to the **general procedure D**, and the product is consistent with previously reported characterization data.[210] ^{19}F NMR (282 MHz, CD_3CN): +118.97 (4F, s).



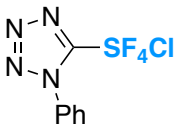
(4-Azidophenyl)chlorotetrafluoro-λ⁶-sulfane (S-2w). The reaction was run according to the **general procedure D**, and the product was converted to the more stable pentafluorosulfanyl arene **S-4f** to obtain complete characterization data. ^{19}F NMR (282 MHz, CD_3CN): +137.77 (4F, s).



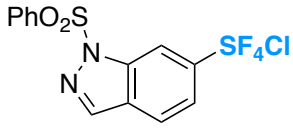
2-(4-(Chlorotetrafluoro-λ⁶-sulfaneyl)phenyl)isoindoline-1,3-dione (S-2x). The reaction was run according to the **general procedure D**, and the product was converted to the more stable pentafluorosulfanyl arene **S-4e** to obtain characterization data. ^{19}F NMR (282 MHz, CD_3CN): +136.81 (4F, s).



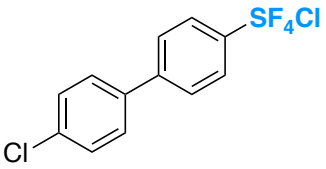
3-(Chlorotetrafluoro-λ⁶-sulfaneyl)-5,6-diphenyl-1,2,4-triazine (S-2y). The reaction was run according to the **general procedure D**; initial attempts to convert the product to the pentafluorosulfanyl arene to obtain complete characterization data were unsuccessful. ^{19}F NMR (282 MHz, CD_3CN): +120.59 (4F, s).



5-(Chlorotetrafluoro-λ⁶-sulfaneyl)-1-phenyl-1H-tetrazole (S-2z). The reaction was run according to the **general procedure D**; initial attempts to convert the product to the pentafluorosulfanyl arene to obtain complete characterization data were unsuccessful. ^{19}F NMR (377 MHz, CD_3CN): *trans*-isomer: 137.81 (4F, s); *cis*-isomer: +145.54 (1F, q, J = 163.5 Hz), +116.93 (2F, dd, J = 163.5, 96.8 Hz), +76.63 (1F, dt, J = 163.5, 96.8 Hz). *trans*:*cis* ratio: 1:2.9.

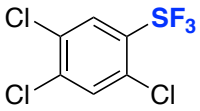


6-(Chlorotetrafluoro-λ⁶-sulfaneyl)-1-(phenylsulfonyl)-1H-indazole (S-2aa). The reaction was run according to the **general procedure D**; initial attempts to convert the product to the pentafluorosulfanyl arene to obtain complete characterization data were unsuccessful. ^{19}F NMR (282 MHz, CD_3CN): +137.59 (4F, s).

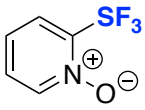


Chloro(4'-chloro-[1,1'-biphenyl]-4-yl)tetrafluoro-λ⁶-sulfane (S-2ab). The reaction was run according to the **general procedure D**, and the product was converted to the more stable pentafluorosulfanyl arene **S-4i** to obtain characterization data. ^{19}F NMR (282 MHz, CD_3CN): +137.13 (4F, s).

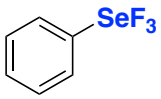
6.2.5 Analytical Data of Aryl-SF_3 and Aryl-SeF_3 Compounds



Trifluoro(2,4,5-trichlorophenyl)-λ⁴-sulfane (S-3a). The reaction was run according to the **general procedure D**; the product was unstable toward isolation during initial attempts and characterized by ^{19}F NMR. ^{19}F NMR (282 MHz, CD_3CN): +63.46 (2F, d, J = 75.6 Hz), -56.31 (1F, t, J = 75.6 Hz).



2-(Trifluoro-λ⁴-sulfaneyl)pyridine 1-oxide (S-3b). The reaction was run according to the **general procedure D**; the product was unstable toward isolation during initial attempts and characterized by ^{19}F NMR. ^{19}F NMR (377 MHz, CD_3CN): +53.58 (2F, d, J = 102.2 Hz), -67.65 (1F, t, J = 102.2 Hz).



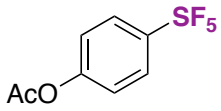
Trifluoro(phenyl)-λ⁴-selane (Se-2a). The reaction was run according to the **general procedure D**; the product was unstable toward isolation during initial attempts and characterized by ^{19}F NMR. The product is consistent with previously reported characterization data.[105] ^{19}F NMR (377 MHz, CD_3CN): -25.51 (3F, br s).

6.2.6 Procedure for the Synthesis of Aryl-SF_5 Compounds

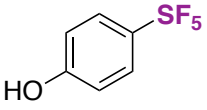
General Procedure E for the reaction of Aryl-SF_4Cl Compounds with AgF

A solution of a known amount of aryl-SF_4Cl compound (1.0 equiv.) in anhydrous DCM was transferred to a copper or PFA vessel and concentrated under inert atmosphere. Subsequently, AgF (2.0 equiv.) was added, and the reactor was sealed under Ar atmosphere. The sealed reactor was heated to 120 °C for ca. 2 days. Upon cooling, the reactor was rinsed with copious amounts of DCM and H_2O into a separatory funnel. The reaction mixture was extracted with DCM. The combined organic layers were dried with $MgSO_4$, filtered through Celite, and concentrated. The crude reaction mixture was purified via gradient column chromatography on silica gel, eluting with n-hexane:EtOAc (20:1 to 5:1 over 20 min).

6.2.7 Specific Procedures and Analytical Data for Aryl-SF_5 Compounds

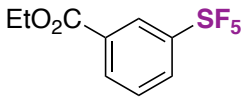


4-(Pentafluoro-λ⁶-sulfaneyl)phenyl acetate (S-4a). The reaction was run according to the **general procedure E** using AgF in a copper vessel; the product was isolated via gradient column chromatography on silica gel in 77% yield (46 mg, 0.18 mmol) as a white solid; m.p. 38.2-39.4 °C. ^{19}F NMR (377 MHz, $CDCl_3$): 84.32 (1F, quint, J = 150.6 Hz), 63.62 (4F, d, J = 150.6 Hz); ^{1}H NMR (400 MHz, $CDCl_3$): 7.78 (2H, dm, J = 9.1 Hz), 7.20 (2H, d, J = 9.1 Hz), 2.33 (3H, s); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): 168.7, 152.5, 150.9 (quint, J = 18.0 Hz), 127.5 (quint, J = 4.8 Hz), 121.8, 21.0. ν_{max} (ATR-IR): 1756 cm^{-1}. HRMS (EI): calc'd for $C_8H_7F_5O_2S$ $[M]^+$: 262.0081, found: 262.0088.

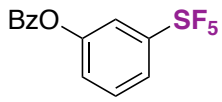


4-(Pentafluoro-λ⁶-sulfaneyl)phenol (S-4b). The reaction was carried out as per the **general procedure E** using 4-(chlorotetrafluoro-λ⁶-sulfaneyl)phenyl acetate **S-2m** (0.14 mmol, quantified by ^{19}F NMR prior to concentration) and AgF (0.28 mmol, 2.0 equiv.) in a copper vessel under Ar atmosphere. The crude reaction mixture was dissolved in ~3:1 MeOH:H_2O and stirred with LiOH (0.71 mmol, 5.0 equiv.) at room temperature for 1 h. The reaction mixture was acidified with 1 M HCl, transferred to a separatory funnel, and extracted with DCM. The combined organic layers were dried with $MgSO_4$, filtered through Celite, and concentrated. The crude reaction mixture was purified via gradient column

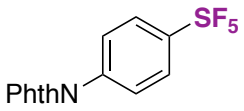
chromatography on silica gel, eluting with n-hexane:EtOAc. The product, 4-(pentafluoro-λ⁶-sulfaneyl)phenol **S-4b**, was obtained as a white solid in 68 % yield (21 mg, 0.10 mmol). m.p. 41.6-42.2 °C. ^{19}F NMR (377 MHz, $CDCl_3$): 86.05 (1F, quint, J = 150.0 Hz), 64.32 (4F, d, J = 150.0 Hz); ^{1}H NMR (400 MHz, $CDCl_3$): 7.65 (2H, dm, J = 9.1 Hz), 6.86 (2H, dm, J = 9.1 Hz), 5.17 (1H, br s). ν_{max} (ATR-IR): 3242 (br) cm^{-1}. HRMS (EI): calc'd for $C_6H_5F_5OS$ $[M]^+$: 219.9976, found: 219.9972. The product is consistent with previously reported characterization data.[211]



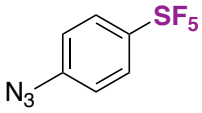
Ethyl 3-(pentafluoro-λ⁶-sulfaneyl)benzoate (S-4c). The reaction was run according to the **general procedure E** using AgF in a copper vessel; the product was isolated via gradient column chromatography on silica gel in 57% yield (20 mg, 0.07 mmol) as a colorless oil. ^{19}F NMR (471 MHz, $CDCl_3$): 83.35 (1F, quint, J = 150.4 Hz), 62.79 (4F, d, J = 150.4 Hz); ^{1}H NMR (500 MHz, $CDCl_3$): 8.43 (1H, m), 8.20 (1H, d, J = 7.8 Hz), 7.94 (1H, m), 7.56 (1H, t, J = 8.0 Hz), 4.43 (2H, q, J = 7.1 Hz), 1.42 (3H, t, J = 7.1 Hz); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 164.8, 153.9 (quint, J = 18.2 Hz), 132.5, 131.5, 130.0 (quint, J = 4.6 Hz), 128.9, 127.2 (quint, J = 4.6 Hz), 61.8, 14.3. ν_{max} (ATR-IR): 1724 cm^{-1}. HRMS (EI): calc'd for $C_9H_9F_5O_2S$ $[M]^+$: 276.0238, found: 276.0237. The product is consistent with previously reported characterization data.[212]



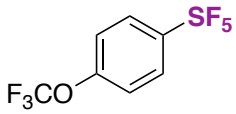
3-(Pentafluoro-λ⁶-sulfaneyl)phenyl benzoate (S-4d). The reaction was run according to the **general procedure E** using 4.0 equiv. AgF in a PFA vessel; the product was isolated via gradient column chromatography on silica gel in 81% yield (23 mg, 0.07 mmol) as a yellow oil. ^{19}F NMR (471 MHz, $CDCl_3$): 83.53 (1F, quint, J = 150.8 Hz), 63.08 (4F, d, J = 150.8 Hz); ^{1}H NMR (500 MHz, $CDCl_3$): 8.22-8.20 (2H, m), 7.70-7.66 (3H, m), 7.56-7.53 (3H, m), 7.44-7.43 (1H, m); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 164.6, 154.3 (quint, J = 18.2 Hz), 150.5, 134.1, 130.3, 129.5, 128.7, 125.3, 123.4 (quint, J = 4.6 Hz), 120.1 (quint, J = 4.6 Hz). ν_{max} (ATR-IR): 1743 cm^{-1}. HRMS (ESI-TOF): calc'd for $C_{13}H_9F_5NaO_2S$ $[M+Na]^+$: 347.0136, found: 347.0131.



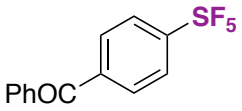
2-(4-(Pentafluoro-λ⁶-sulfaneyl)phenyl)isoindoline-1,3-dione (S-4e). The reaction was run according to the **general procedure E** using 4.0 equiv. AgF in a PFA vessel; the product was isolated via gradient column chromatography on silica gel in 80% yield (6.9 mg, 0.02 mmol) as a white solid; m.p. 217.2-219.0 °C. ^{19}F NMR (471 MHz, $CDCl_3$): 83.79 (1F, quint, J = 150.5 Hz), 63.14 (4F, d, J = 150.5 Hz); ^{1}H NMR (500 MHz, $CDCl_3$): 7.99 (2H, dd, J = 5.4, 3.1 Hz), 7.90 (2H, d, J = 9.1 Hz), 7.84 (2H, dd, J = 5.4, 3.1 Hz), 7.65 (2H, d, J = 9.1 Hz); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 166.6, 152.5 (quint, J = 18.2 Hz), 134.8, 134.6, 131.4, 126.9 (quint, J = 4.5 Hz), 126.1, 124.1. ν_{max} (ATR-IR): 1720, 1711, 1702 cm^{-1}. HRMS (ESI- TOF): calc'd for $C_{14}H_9F_5NO_2S$ $[M+H]^+$: 350.0269, found: 350.0268. Single crystals suitable for X-ray analysis were obtained by solvent evaporation ($CDCl_3$). The product is consistent with previously reported characterization data.[103]



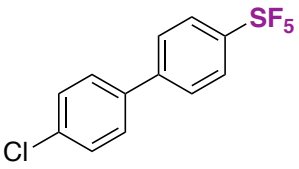
(4-Azidophenyl)pentafluoro-λ⁶-sulfane (S-4f). The reaction was run according to the **general procedure E** using AgF in a PFA vessel; the product was isolated via gradient column chromatography on silica gel in 63% yield (21.3 mg, 0.09 mmol) as a light yellow oil. ^{19}F NMR (471 MHz, $CDCl_3$): 84.59 (1F, quint, J = 150.8 Hz), 63.67 (4F, quint, J = 150.8 Hz); ^{1}H NMR (500 MHz, $CDCl_3$): 7.74 (2H, d, J = 9.0 Hz), 7.08 (2H, d, J = 9.0 Hz). The product is consistent with previously reported characterization data.[213]



Pentafluoro(4-(trifluoromethoxy)phenyl)-λ⁶-sulfane (S-4g). The reaction was run according to the **general procedure E** using AgF in a PFA vessel at 100 °C; the product was too volatile for small-scale isolation. Thus, yield determination and characterization are by ^{19}F NMR only. ^{19}F NMR (471 MHz, $CDCl_3$): 83.45 (1F, quint, J = 150.5 Hz), 63.47 (4F, d, J = 150.5 Hz).



(4-(Pentafluoro-λ⁶-sulfaneyl)phenyl)(phenyl)methanone (S-4h). The reaction was run according to the **general procedure E** using AgF in a PFA vessel; the product was isolated via gradient column chromatography on silica gel in 57% yield (18 mg, 0.06 mmol) as a white solid; m.p. 116.4-117.3 °C. ^{19}F NMR (377 MHz, $CDCl_3$): 83.11 (1F, quint, J = 150.4 Hz), 62.64 (4F, d, J = 150.4 Hz); ^{1}H NMR (400 MHz, $CDCl_3$): 7.90-7.85 (4H, m), 7.82-7.79 (2H, m), 7.66-7.62 (1H, tm, J = 7.4 Hz), 7.54-7.49 (2H, m); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 194.9, 156.2 (quint, J = 18.1 Hz), 140.3, 136.5, 133.3, 130.09, 130.08, 128.6, 126.1 (quint, J = 4.7 Hz). ν_{max} (ATR-IR): 1653 cm^{-1}. HRMS (EI): calc'd for $C_{13}H_9F_5OS$ $[M]^+$: 308.0289, found: 308.0282. Single crystals suitable for X-ray analysis were obtained by sublimation.



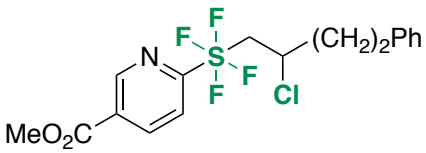
(4'-Chloro-[1,1'-biphenyl]-4-yl)pentafluoro-λ⁶-sulfane (S-4i). The reaction was run according to the **general procedure E** using AgF in a PFA vessel; the product was isolated via gradient column chromatography on silica gel in 77% yield (29 mg, 0.92 mmol) as a white solid; m.p. 82.8-84.8 °C. ^{19}F NMR (471 MHz, $CDCl_3$): +84.60 (1F, quint, J = 150.2 Hz), +63.24 (4F, d, J = 150.2 Hz); ^{1}H NMR (500 MHz, $CDCl_3$): 7.83 (2H, dm, J = 8.6 Hz), 7.62 (2H, br d, J = 8.6 Hz), 7.52 (2H, dm, J = 8.6 Hz), 7.45 (2H, dm, J = 8.6 Hz); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 153.1 (quint, J = 17.5 Hz), 143.3, 137.5, 134.8, 129.3, 128.5, 127.1, 126.6 (quint, J = 4.6 Hz). ν_{max} (ATR-IR): 840 cm^{-1} (br), 813 cm^{-1}. HRMS (EI): calc'd for $C_{12}H_8ClF_5S$ $[M]^+$: 313.9950, found 313.9947. Single crystals suitable for X-ray analysis were obtained by sublimation.

6.2.8 Procedures for the Synthesis of Aryl-SF_4R Compounds[99,104]

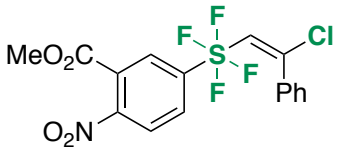
General Procedure F for the reaction of Aryl-SF_4Cl Compounds with BEt3 and alkenes/alkynes

A solution of a known amount of aryl-SF_4Cl compound (1.0 equiv.) in anhydrous DCM (0.05- 0.1 M) was transferred to a PFA vessel equipped with a stir bar under Ar atmosphere. The alkene or alkyne substrate (1.5 equiv.) was added, followed by 10 mol % BEt_3 (administered as a 1.0 M solution in n-hexane), and the reaction mixture was stirred at room temperature for 1 h. At this time, the reaction mixture was quenched with saturated aq. $NaHCO_3$ and extracted into DCM. The combined organic layers were dried with $MgSO_4$, filtered through Celite, and concentrated. The crude reaction mixture was purified via gradient column chromatography on silica gel, eluting with *n*-hexane:EtOAc.

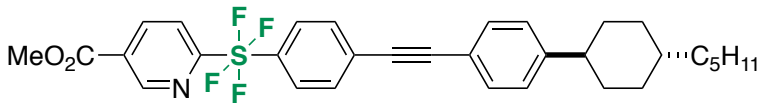
6.2.9 Specific Procedures and Analytical Data for Aryl-SF_4R Compounds



Methyl 6-((2-chloro-4-phenylbutyl)tetrafluoro-λ⁶-sulfaneyl)nicotinate (S-5a). The reaction was run according to the **general procedure F** using 4-phenyl-1-butene and BEt_3; the product was isolated via gradient column chromatography on silica gel in 84% yield (25 mg, 0.06 mmol) as a white solid. ^{19}F NMR (377 MHz, $CDCl_3$): 57.59 (4F, t, J = 8.5 Hz, becomes s in $^{19}F\{^1H\}$ spectrum); ^1H NMR (400 MHz, $CDCl_3$): 9.10 (1H, d, J = 2.1 Hz), 8.44 (1H, d, J = 8.5 Hz), 7.80 (1H, d, J = 8.5 Hz), 7.34-7.21 (5H, m), 4.60-4.54 (1H, m), 4.46-4.34 (1H, m, becomes dd, J = 13.7, 5.3 Hz in $^1H\{^{19}F\}$ spectrum), 4.33-4.20 (1H, m, becomes dd, J = 13.7, 7.2 Hz in $^1H\{^{19}F\}$ spectrum), 4.00 (3H, s), 3.00 (1H, ddd, J = 14.0, 9.2, 4.5 Hz), 2.87-2.80 (1H, m), 2.52-2.44 (1H, m), 2.18-2.08 (1H, m); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): 172.6 (quint, J = 31.7 Hz), 164.3, 148.6 (m), 140.2, 139.6, 128.53, 128.49, 127.9, 126.3, 121.1 (quint, J = 4.8 Hz), 81.6 (quint, J = 18.7 Hz), 56.5 (quint, J = 5.2 Hz), 52.8, 39.2, 32.3. Single crystals suitable for X-ray analysis were obtained by solvent evaporation (mixture of *n*-hexane and benzene). Although this product proved stable toward column chromatography, note that it degraded after a few days in $CDCl_3$ solution in the NMR tube.



Methyl (E)-5-((2-chloro-2-phenylvinyl)tetrafluoro-λ⁶-sulfaneyl)-2-nitrobenzoate (S-5b). The reaction was run according to the **general procedure F** using phenylacetylene and BEt_3; the product was isolated via gradient column chromatography on silica gel in 70 % yield (40 mg, 0.09 mmol) as a white solid. ^{19}F NMR (282 MHz, CD_3CN): 71.26 (4F, d, *J* = 8.4 Hz, becomes s in $^{19}F\{^1H\}$ spectrum); ^1H NMR (400 MHz, $CDCl_3$): 8.01 (1H, dm, *J* = 2.2 Hz), 7.86 (1H, dd, *J* = 8.9, 2.2 Hz), 7.81 (1H, dm, *J* = 8.9 Hz), 7.43-7.38 (5H, m), 7.18 (1H, quint, *J* = 8.4 Hz), 3.91 (3H, s); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): 164.2, 161.7 (quint, *J* = 27.6 Hz), 148.6, 143.0 (quint, *J* = 28.6 Hz), 139.8 (quint, *J* = 7.8 Hz), 136.5, 129.7 (quint, *J* = 5.4 Hz), 129.5, 128.1, 127.9 (m), 127.2, 123.8, 53.6. Although this product proved stable toward column chromatography, note that it degraded after a few days in $CDCl_3$ solution in the NMR tube.



Methyl 6-(tetrafluoro(4-((4-((1s,4r)-4-pentylcyclohexyl)phenyl)ethynyl)phenyl)-λ⁶-sulfaneyl)nicotinate (S-5c). A solution of a methyl 6-(chlorotetrafluoro-λ⁶-sulfanyl)nicotinate **S-2p** (0.15 mmol, 1.0 equiv.) in 5 mL anhydrous DCM was transferred to a PFA vessel equipped with a stir bar under Ar atmosphere. Subsequently, 1-ethynyl-4-(*trans*-4 pentylcyclohexyl)benzene (42 mg, 0.17 mmol, 1.1 equiv.) was added, followed by 20 mol % BEt_3 (0.03 mL, 0.03 mmol, administered as a 1.0 M solution in n-hexane), and the reaction mixture was stirred at room temperature overnight. After this time, the reaction mixture was quenched with saturated aq. $NaHCO_3$ and extracted into DCM. The combined organic layers were dried with $MgSO_4$, filtered through Celite, and concentrated. The crude reaction mixture was purified via gradient column chromatography on silica gel, eluting with n-hexane:EtOAc. The aryl tetrafluoro-λ⁶-sulfanyl chloride alkene intermediate was obtained as a white solid in 68 % yield (54 mg, 0.10 mmol). Subsequently, the aryl tetrafluoro-λ⁶-sulfanyl chloride alkene intermediate (11 mg, 0.02 mmol, 1.0 equiv.) was added to an oven-dried microwave vial equipped with a stir bar, along with LiOMe (7.8 mg, 0.20 mmol, 10 equiv.). The vial was sealed with a cap with septum using a crimper, and the sealed vial was evacuated and refilled with Ar multiple times. Then, 1.3 mL DMSO-d_6 was added, and the reaction mixture was stirred at room temperature. An aliquot after 48 h was taken for NMR analysis; this revealed near quantitative conversion of the aryl tetrafluoro-

λ⁶-sulfanyl chloride alkene intermediate to the desired aryl tetrafluoro-λ⁶-sulfanyl alkyne **S-5c**. The product was characterized by NMR analyses in DMSO-d_6 directly from the reaction mixture. ^{19}F NMR (377 MHz, DMSO-d_6): +78.44 (4F, s); ^{1}H NMR (400 MHz, (CD3)2SO): 8.83 (1H, d, *J* = 2.1 Hz), 8.35 (1H, ddm, *J* = 8.4, 2.1 Hz; determined from ^{1}H{^{19}F} spectrum), 7.78 (1H, d, *J* = 8.4 Hz), 7.58 (2H, d, *J* = 8.3 Hz), 7.35 (2H, d, *J* = 8.3 Hz), 4.13 (1H, q, *J* = 5.3 Hz), 3.17-3.15 (3H, m), 1.83-1.78 (4H, m), 1.49-1.38 (2H, m), 1.33-1.17 (9H, m), 1.08-0.98 (2H, m), 0.87 (3H, t, *J* = 7.0 Hz); ^{13}C {^{1}H} NMR (101 MHz, (CD3)2SO): 169.9, 150.8, 148.2 (m), 139.5, 139.1, 132.4, 127.5, 119.7 (m), 73.43 (m), 48.6, 43.8, 36.8, 36.5, 33.4, 32.9, 31.6, 26.0, 22.1, 13.9. *Note: quintets of the aryl and alkynyl carbon atoms adjacent to -SF4- unit were not resolved.*

6.3 Experimental Details to Chapter 3

6.3.1 Procedures for Syntheses of Telluride Starting Materials

The synthesis of diaryl ditelluride was achieved following literature procedures.[132–135] Apart from novel molecules **Te-1f**, **Te-1g**, **Te-1k** and **Te-1l** the known ditellurides were not thoroughly analyzed and so their characterization data is not reported herein as they had been accessed and characterized by other groups before. Their purity was typically confirmed by ^{1}H NMR. Ditelluride starting material for the synthesis of **Te-2a** is commercially available, was bought and used as received.

General Procedure G for Starting Materials of Compounds Te-2b–Te-2f[132]

Mg turnings (0.12 g, 10 mmol, 1.0 eq.) were heated under Ar in an oven-dried 100 mL two-necked round-bottom flask equipped with a stir bar and a drop funnel. After cooling to rt, dry THF (20 mL) was added. The corresponding aryl halide (10 mmol, 1.0 eq.) was added dropwise to the stirred suspension. The solution was stirred for 1 h, and Te powder (1.9 g, 15 mmol, 1.9 eq.) was then added. The resulting suspension was stirred for 1 h, after which its color had changed to dark green. The reaction mixture was quenched by the addition of saturated aq. NH_4Cl solution (10 mL) and was stirred open to air overnight, resulting in oxidation of the intermediate to the deep red ditelluride. The crude product was extracted with DCM (3 x 20 mL), and the organic phases were combined, dried with Na_2SO_4, filtered through Celite, and concentrated in vacuo to yield the crude ditelluride, which was purified by flash column chromatography eluting with n-hexane. Note that compound **Te-2f** was recrystallized from EtOH.

General Procedure H for Starting Materials of Compound Te-2j[134,135]

Under Ar atmosphere, a dry Schlenk tube equipped with a stir bar and a rubber septum was charged with Te powder (1.26 g, 10 mmol, 2.0 eq.), $NaBH_4$ (0.45 g, 12 mmol, 2.4 eq.), and dry DMF (20 mL). The mixture was heated to 85 °C for 1 h, and 4-iodobenzophenone (1.54 g, 5.0 mmol, 1.0 eq.) was then added under an Ar counter stream in one portion. The reaction mixture was stirred at 85 °C for 8 h, quenched with H_2O (20 mL), and stirred open to air overnight, resulting in oxidation of the intermediate to the deep red ditelluride. The mixture was then filtered through Celite and extracted with benzene (3 x 15 mL). The combined organic phases were dried with Na_2SO_4, filtered through Celite, and concentrated in vacuo to afford the crude ditelluride, which was recrystallized from EtOH to yield the corresponding ditelluride (220 mg, 0.4 mmol, 14%).

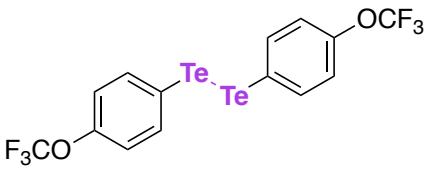
General Procedure I for Starting Materials of Compounds Te-2g–Te-2i, Te-2k and Te-2l[133]

Under Ar atmosphere, a dry Schlenk tube equipped with a stir bar and a drop funnel was charged with aryl halide (5.0 mmol, 1.0 eq.) and dry THF (50 mL). The reaction mixture was cooled to -78°C, and ^{t}BuLi (1.7 M solution, 4.4 mL, 7.5 mmol, 1.5 eq.) was added dropwise using the drop funnel (upon addition, the color of the reaction mixture changes to a deep orange). The reaction mixture was stirred for 1 h at low temperature, and Te powder (989 mg, 7.75 mmol, 1.55 eq.) was added in one portion. The cooling bath was removed, and stirring was continued for 4 h at rt (the color of the reaction mixture changes to red). The reaction mixture was quenched by pouring the contents of the Schlenck tube into an Erlenmeyer flask (300 mL) equipped with a stir bar containing an ice/water mixture (100 mL). The resulting black suspension was stirred open to air overnight. The reaction mixture was then extracted with DCM (5 x 50 mL), and the combined organic phases were dried with Na_2SO_4 and filtered through Celite. The resulting transparent red/orange solution was filtered through basic alumina and concentrated in vacuo to afford the corresponding ditelluride, which was purified by flash column chromatography eluting with n-hexane. Note that compounds **Te-2g** and **Te-2l** were recrystallized from EtOH and MeCN, respectively.

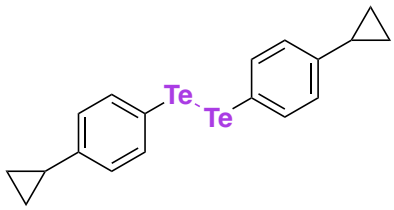
General Procedure J for Starting Materials of Compounds Te-4a and Te-4b[137]

The corresponding ditelluride (2.1 mmol, 1.0 eq.) was added to a dry Schlenk tube equipped with a stir bar. The flask was evacuated and refilled with argon three times. Under a counter stream of Ar, 3,3-dimethyl-1-(trifluoromethyl)-1,3-dihydro-1λ^3-benzo[*d*][1,2]iodaoxole (0.73 g, 2.2 mmol, 1.05 eq.) was added in one portion. The mixture was dissolved in DCM (2 mL) and was stirred for 1 h at 50 °C. The solvent was removed under a stream of Ar, and the crude red oil was purified by Kugelrohr distillation to afford the corresponding aryl-$TeCF_3$ compound. The compounds were not fully characterized as they've been accessed before.

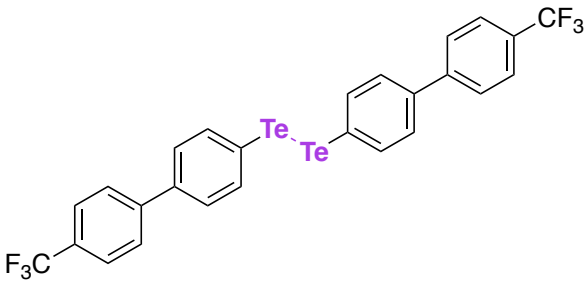
6.3.2 Analytical Data of Novel Ditellurides



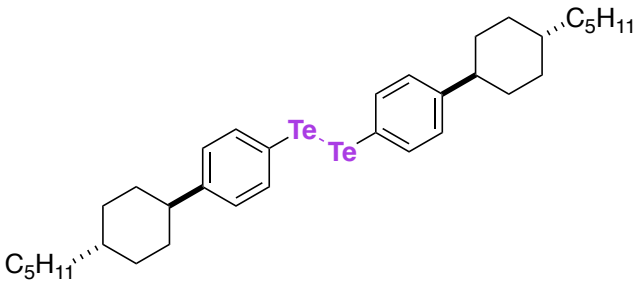
1,2-Bis(4-(trifluoromethoxy)phenyl)ditellane (Te-2f). The reaction was run according to the **general procedure G** outlined above. Orange solid; m.p. 57.7-58.6 °C. ^{19}F NMR (471 MHz, $CDCl_3$): -57.69 (6F, s); ^{1}H NMR (500 MHz, $CDCl_3$): 7.79 (4H, d, J = 7.8 Hz), 7.05 (4H, d, J = 7.8 Hz); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): 150.0, 139.7, 122.2, 120.9 (q, J = 257.3 Hz), 105.8. HRMS (EI): calc'd for $C_{14}H_8F_6O_2Te_2$ [M]$^+$: 581.8549, found 581.8548.



1,2-Bis(4-cyclopropylphenyl)ditellane (Te-2g). The reaction was run according to the **general procedure I** outlined above. Red solid; m.p. 98.7-99.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.67 (4H, d, J = 8.2 Hz), 6.89 (4H, d, J = 8.2 Hz), 1.90-1.84 (2H, m), 1.00-0.95 (4H, m), 0.70-0.66 (4H, m); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 144.6, 138.1, 126.6, 103.9, 15.1, 9.6. HRMS (EI): calc'd for $C_{18}H_{18}Te_2$ [M]$^+$: 493.9529, found 493.9531.



1,2-Bis(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)ditellane (Te-2k). The reaction was run according to the **general procedure I** outlined above. Red solid; m.p. 218-219 °C. ^{19}F NMR (471 MHz, $CDCl_3$): -62.33 (6F, s); ^{1}H NMR (500 MHz, $CDCl_3$): 7.92 (4H, d, J = 8.3 Hz), 7.70 (4H, d, J = 8.4 Hz), 7.66 (4H, d, J = 8.4 Hz), 7.43 (4H, d, J = 8.3 Hz); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): 144.2, 140.0, 139.1, 138.6, 129.8 (q, J = 32.2 Hz), 128.4, 127.8, 126.1 (q, J = 3.7 Hz), 124.8 (q, J = 271.9 Hz). HRMS (EI): calc'd for $C_{26}H_{16}F_6Te_2$ [M]$^+$: 701.9279, found 701.9284.



1,2-Bis(4-((1s,4r)-4-pentylcyclohexyl)phenyl)ditellane (Te-2l). The reaction was run according to the **general procedure I** outlined above. Red solid; m.p. 94.5-95.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 7.71 (4H, d, *J* = 8.1 Hz), 7.04 (4H, d, *J* = 8.1 Hz), 2.45 (2H, tt, *J* = 12.3, 2.8 Hz), 1.88-1.84 (8H, m), 1.47-1.36 (4H, m), 1.36-1.18 (18H, m), 1.08-0.98 (4H, m), 0.90 (6H, t, *J* = 7.0 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 148.2, 137.8, 128.0, 104.4, 44.3, 37.34, 37.26, 34.3, 33.5, 32.2, 26.7, 22.7, 14.1. HRMS (EI): calc'd for $C_{34}H_{51}Te_2$ $[M]^+$: 719.2116, found 719.2103.

6.3.3. Procedures for the Synthesis of Aryl-TeF_5 and Aryl-TeF_4CF_3 Compounds

General Procedure K for the Reaction of Diaryl Ditellurides with TCICA/KF

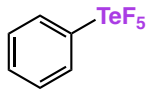
Trichloroisocyanuric acid (0.64 g, 2.7 mmol, 6.0 equiv.) was added to an oven-dried microwave vial equipped with a stir bar; the vessel was then transported inside a glove box under N_2 atmosphere. Spray-dried (or crushed and rigorously dried) potassium fluoride (0.64 g, 11 mmol, 24 equiv.) and the diaryl ditelluride substrate (0.46 mmol, 1.0 equiv.) were added to the reaction vessel, which was then sealed with a cap w/ septum. The closed vial was removed from the glove box. Under Ar atmosphere, 8 mL anhydrous MeCN was added to the vessel, followed by trifluoroacetic acid (3.6 mL, 0.05 mmol, 0.1 equiv.). The reaction mixture was stirred vigorously at room temperature overnight (ca. 16 h). Subsequently, the crude reaction mixture was filtered into a PFA vessel via syringe filter and concentrated in vacuo. The crude reaction mixture was diluted with dry n-hexane, filtered into another PFA vessel, and concentrated in vacuo to afford the pure **aryl-TeF_5** products. (*Note that repeating dilution and filtration multiple times prior to concentration may provide better yields.*)

General Procedure L for the Reaction of Aryl(trifluoromethyl)tellurides with TCICA/KF

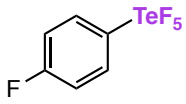
Trichloroisocyanuric acid (0.64 g, 2.7 mmol, 6.0 equiv.) was added to an oven-dried microwave vial equipped with a stir bar; the vessel was then transported inside a glove box under N_2 atmosphere. Spray-dried (or crushed and rigorously dried) potassium fluoride (0.64 g, 11 mmol, 24 equiv.) and the aryl(trifluoromethyl)tellane substrate (0.46 mmol, 1.0

equiv.) were added to the reaction vessel, which was then sealed with a cap w/ septum. The closed vial was removed from the glove box. Under Ar atmosphere, 8 mL anhydrous MeCN was added to the vessel, followed by trifluoroacetic acid (3.6 μL, 0.05 mmol, 0.1 equiv.). The reaction mixture was stirred vigorously at room temperature overnight (ca. 16 h). Subsequently, the crude reaction mixture was filtered into a PFA vessel via syringe filter and concentrated in vacuo. The crude reaction mixture was diluted with dry n-hexane, filtered into another PFA vessel, and concentrated in vacuo to afford the pure the **aryl-TeF_4CF_3** products. (*Note that repeating dilution and filtration multiple times prior to concentration may provide better yields.*)

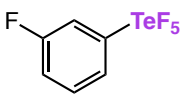
6.3.4 Analytical Data of Aryl-TeF_5 and Aryl-TeF_4CF_3 Compounds



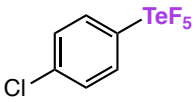
Pentafluoro(phenyl)-λ⁶-tellane (Te-2a). The reaction was run according to the **general procedure K**, and the product is consistent with previously reported characterization data. Colorless oil. ^{19}F NMR (282 MHz, $CDCl_3$): -37.11 (1F, quint, J = 150.6 Hz), -53.39 (4F, d, J = 150.6 Hz); ^{1}H NMR (400 MHz, $CDCl_3$): 7.92 (2H, d, J = 8.1 Hz), 7.83-7.78 (1H, m), 7.75-7.70 (2H, m); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): 142.2-141.9 (m), 135.4, 131.4 (quint, J = 1.5 Hz), 130.3 (quint, J = 2.2 Hz). ν_{max} (ATR-IR): 655 cm^{-1} (br). HRMS (EI): calc'd for $C_6H_5F_5Te$ $[M]^+$: 301.9374, found: 301.9374.



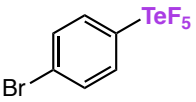
Pentafluoro(4-fluorophenyl)-λ⁶-tellane (Te-2b). The reaction was run according to the **general procedure K**. Light yellow oil. ^{19}F NMR (282 MHz, $CDCl_3$): -37.02 (1F, quint, J = 151.7 Hz), -51.94 (4F, d, J = 151.7 Hz), -98.44 (1F, m); ^{1}H NMR (300 MHz, $CDCl_3$): 7.97 (2H, dd, J = 8.9, 4.7 Hz), 7.43 (2H, m); $^{13}C\{^{1}H\}$ NMR (76 MHz, $CDCl_3$): 166.5 (d, J = 260.1 Hz), 136.6 (m), 133.1 (dquint, J = 9.7, 2.5 Hz), 118.8 (dquint, J = 23.1, 1.7 Hz). ν_{max} (ATR-IR): 666 cm^{-1} (br). HRMS (EI): calc'd for $C_6H_4F_6Te$ $[M]^+$: 319.9274, found: 319.9273.



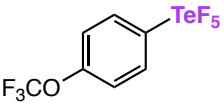
Pentafluoro(3-fluorophenyl)-λ⁶-tellane (Te-2c). The reaction was run according to the **general procedure K**. Colorless oil. ^{19}F NMR (471 MHz, CD_3CN): -38.42 (1F, quint, J = 149.4 Hz), -53.93 (4F, d, J = 149.4 Hz), -106.22 (1F, m); ^{1}H NMR (500 MHz, CD_3CN): 7.93-7.84 (3H, m), 7.72-7.69 (3H, m); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3CN): 164.0 (dquint, J = 255.1, 2.7 Hz), 141.9-141.5 (m), 134.7 (dquint, J = 8.2, 1.8 Hz), 127.7-127.6 (m), 124.9 (d, J = 20.9 Hz), 118.9 (dm, J = 26.3). ν_{max} (ATR-IR): 672 cm^{-1} (br). HRMS (EI): calc'd for $C_6H_4F_6Te$ $[M]^+$: 319.9274, found 319.9276.



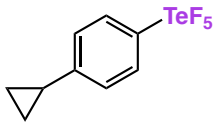
(4-Chlorophenyl)pentafluoro-λ⁶-tellane (Te-2d). The reaction was run according to the **general procedure K**. Clear solid; m.p. 75.4-76.3 °C. ^{19}F NMR (282 MHz, $CDCl_3$): -37.25 (1F, quint, *J* = 151.7 Hz), -52.22 (4F, d, *J* = 151.7 Hz); ^{1}H NMR (400 MHz, $CDCl_3$): 7.88 (2H, d, *J* = 8.7 Hz), 7.71 (2H, dquint, *J* = 8.7, 1.5 Hz); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): 142.6, 139.6 (quintd, *J* = 8.5, 2.6 Hz), 131.53 (m), 131.47. ν_{max} (ATR-IR): 656 cm^{-1} (br). HRMS (EI): calc'd for $C_6H_4ClF_5Te$ $[M]^+$: 335.8978, found: 335.8967. Additionally, single crystals suitable for X-ray analysis were obtained by solvent evaporation at rt open to air using a mixture of DCM and n-hexane.



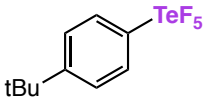
(4-Bromophenyl)pentafluoro-λ⁶-tellane (Te-2e). The reaction was run according to the **general procedure K**. Waxy white solid. ^{19}F NMR (377 MHz, $CDCl_3$): -37.27 (1F, quint, *J* = 151.8 Hz), -52.28 (4F, d, *J* = 151.8 Hz); ^{1}H NMR (400 MHz, $CDCl_3$): 7.87 (2H, dquint, *J* = 8.8, 1.5 Hz), 7.79 (2H, d, *J* = 8.8 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 140.3 (quintd, *J* = 8.8, 2.9 Hz), 134.4 (m), 131.5 (quint, *J* = 2.3 Hz), 131.1. ν_{max} (ATR-IR): 654 cm^{-1} (br). HRMS (EI): calc'd for $C_6H_4BrF_5Te$ $[M]^+$: 379.8473, found: 379.8453. Additionally, single crystals suitable for X-ray analysis were obtained by solvent evaporation at rt open to air using diisopropyl ether.



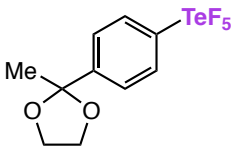
Pentafluoro(4-(trifluoromethoxy)phenyl)-λ⁶-tellane (Te-2f). The reaction was run according to the **general procedure K**. Colorless oil. ^{19}F NMR (377 MHz, $CDCl_3$): -37.42 (1F, quint, *J* = 152.0 Hz), -51.96 (4F, d, *J* = 152.0 Hz), -57.61 (3F, s); ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (2H, d, *J* = 8.9 Hz), 7.55 (2H, dm, *J* = 8.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 154.1 (q, *J* = 2.2 Hz), 138.7 (quintd, *J* = 9.2, 2.9 Hz), 132.6 (quint, *J* = 2.5 Hz), 122.7 (m), 120.1 (q, *J* = 262.2 Hz). ν_{max} (ATR-IR): 672 cm^{-1} (br). HRMS (EI): calc'd for $C_7H_4OF_8Te$ $[M]^+$: 385.9191, found: 385.9192.



(4-Cyclopropylphenyl)pentafluoro-λ⁶-tellane (Te-2g). The reaction was run according to the **general procedure K**. White solid; m.p. 76.8-77.6 °C. ^{19}F NMR (377 MHz, CD_3CN): -36.95 (1F, quint, J = 148.6 Hz), -54.27 (4F, d, J = 148.6 Hz); ^{1}H NMR (400 MHz, CD_3CN): 7.85 (2H, d, J = 8.8 Hz), 7.48 (2H, dquint, J = 8.8, 1.8 Hz), 2.11-2.04 (1H, m), 1.20-1.15 (2H, m), 0.88-0.84 (2H, m); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 155.8, 138.3 (quintd, J = 5.9, 2.9 Hz), 131.1 (quint, J = 2.2 Hz), 129.5 (quint, J = 1.5 Hz), 16.4, 12.0. ν_{max} (ATR-IR): 652 cm^{-1} (br). HRMS (EI): calc'd for $C_9H_9F_5Te$ [M]$^+$: 341.9681, found 341.9679. Additionally, single crystals suitable for X-ray analysis were obtained by solvent evaporation at rt under inert atmosphere using MeCN.

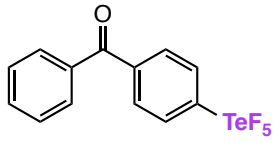


(4-(Tert-butyl)phenyl)pentafluoro-λ⁶-tellane (Te-2h). The reaction was run according to the **general procedure K**. Note that we were unable to isolate an analytically pure sample. White solid. ^{19}F NMR (377 MHz, $CDCl_3$): -36.49 (1F, quint, J = 150.8 Hz), -53.11 (4F, d, J = 150.8 Hz); ^{1}H NMR (400 MHz, $CDCl_3$): 7.83 (2H, d, J = 8.8 Hz), 7.71 (2H, dquint, J = 8.8, 1.7 Hz), 1.37 (9H, s). *Note: we were unable to isolate compound from unidentified byproducts; thus, the ^{13}C{^{1}H} NMR spectrum could not be assigned.* ν_{max} (ATR-IR): 661 cm^{-1} (br). HRMS (EI): calc'd for $C_{10}H_{13}F_5Te$ [M]$^+$: 357.9994, found: 357.9987.

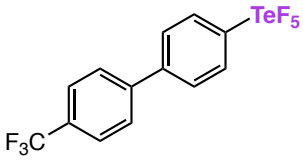


2-Methyl-2-(4-(pentafluoro-λ⁶-tellaneyl)phenyl)-1,3-dioxolane (Te-2i). The reaction was run according to the **general procedure K**. White solid; m.p. 86.2-86.9 °C. ^{19}F NMR (377 MHz, CD_3CN): -37.57 (1F, quint, J = 148.4 Hz), -54.25 (4F, d, J = 148.4 Hz); ^{1}H NMR (400 MHz, CD_3CN): 8.00 (2H, d, J = 8.7 Hz), 7.91 (2H, dquint, J = 8.7, 1.8 Hz), 4.10-4.02 (2H, m), 3.80-3.71 (2H, m), 1.63 (3H, s); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): 153.5, 141.2 (quintd, J = 5.9, 2.9 Hz), 131.2 (quint, J = 2.2 Hz), 129.9 (quint, J = 1.5 Hz), 108.5, 65.6, 27.4. ν_{max} (ATR-IR): 661 cm^{-1} (br). HRMS (EI): calc'd for $C_9H_8O_2F_5Te$ [M]$^+$:

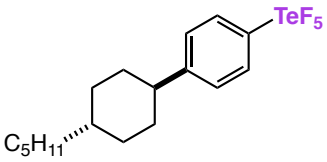
372.9501, found: 372.9502. Additionally, single crystals suitable for X-ray analysis were obtained by solvent evaporation at rt under inert atmosphere using MeCN.



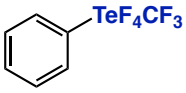
(4-(Pentafluoro-λ⁶-tellaneyl)phenyl)(phenyl)methanone (Te-2j). The reaction was run according to the **general procedure K**. White solid; m.p. 94.2-96.4 °C. ^{19}F NMR (377 MHz, CD_3CN): -38.28 (1F, quint, J = 148.6 Hz), -54.16 (4F, d, J = 148.6 Hz); ^{1}H NMR (400 MHz, CD_3CN): 8.16 (2H, br d, J = 8.6 Hz), 8.10 (2H, dquint, J = 8.6, 1.7 Hz), 7.84-7.81 (2H, m), 7.73 (1H, tm, J = 7.5 Hz), 7.61-7.56 (2H, m); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): 195.3, 145.4, 144.5-144.2 (m), 136.9, 134.7, 133.3 (quint, J = 1.5 Hz), 131.5 (quint, J = 2.2 Hz), 131.07, 129.7. ν_{max} (ATR-IR): 1664 cm^{-1}, 662 cm^{-1} (br). HRMS (EI): calc'd for $C_{13}H_9F_5OTe$ $[M]^+$: 405.9630, found: 405.9632. Additionally, single crystals suitable for X-ray analysis were obtained by solvent evaporation at rt open to air using a mixture of DCM and n-hexane.



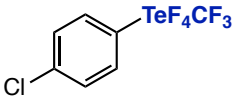
Pentafluoro(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)-λ⁶-tellane (Te-2k). The reaction was run according to the **general procedure K**. White solid; m.p. 127.6-128.6 °C. ^{19}F NMR (377 MHz, CD_3CN): -37.64 (1F, quint, J = 148.3 Hz), -54.03 (4F, d, J = 148.3 Hz), -63.10 (3F, s); ^{1}H NMR (400 MHz, CD_3CN): 8.16-8.10 (4H, m), 7.92 (2H, dm, J = 8.4 Hz), 7.87 (2H, dm, J = 8.4 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 147.1, 141.7, 141.3 (quintd, J = 7.3, 2.7 Hz), 131.4 (q, J = 32.7 Hz), 130.9 (quint, J = 2.2 Hz), 129.9, 127.9, 126.3 (q, J = 3.7 Hz), 123.9 (q, J = 272.1 Hz). ν_{max} (ATR-IR): 665 cm^{-1} (br). HRMS (EI): calc'd for $C_{13}H_8F_8Te$ $[M]^+$: 445.9555, found 445.9554. Additionally, single crystals suitable for X-ray analysis were obtained by solvent evaporation at rt under inert atmosphere using MeCN.



Pentafluoro(4-((1s,4r)-4-pentylcyclohexyl)phenyl)-λ⁶-tellane (Te-2l). The reaction was run according to the **general procedure K**. Clear, amorphous material. ^{19}F NMR (377 MHz, CD_3CN): -37.15 (1F, quint, J = 148.1 Hz), -54.37 (4F, d, J = 148.1 Hz); ^{1}H NMR (400 MHz, CD_3CN): 7.92 (2H, br d, J = 8.6 Hz), 7.69 (2H, dquint, J = 8.6, 1.8 Hz), 2.69 (1H, tt, J = 12.2, 3.2 Hz), 1.94-1.84 (4H, m), 1.56-1.46 (2H, m), 1.40-1.22 (9H, m), 1.14-1.04 (2H, m), 0.91 (3H, t, J = 7.0 Hz); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 158.4, 139.3-139.1 (m), 131.5 (br s), 131.2 (quint, J = 2.2 Hz), 45.3, 38.0, 37.8, 34.5, 33.9, 32.9, 27.3, 23.4, 14.4. ν_{max} (ATR-IR): 664 cm^{-1} (br).



Tetrafluoro(phenyl)(trifluoromethyl)-λ⁶-tellane (Te-4a). The reaction was run according to the **general procedure L**. Light yellow oil. ^{19}F NMR (377 MHz, CD_3CN): -54.17 (3F, quint, J = 21.8 Hz), -68.75 (4F, q, J = 21.8 Hz); ^{1}H NMR (400 MHz, CD_3CN): 8.03 (2H, dm, J = 8.2 Hz), 7.91 (1H, tm, J = 7.5 Hz), 7.86-7.80 (2H, m); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): 142.7 (quint, J = 8.6 Hz), 137.0, 132.7, 131.1 (quint, J = 2.2 Hz). *Note: ^{13}C NMR signal for "CF_3" was not resolved.* ν_{max} (ATR-IR): 625 cm^{-1} (br). HRMS (EI): calc'd for $C_7H_5F_7Te$ $[M]^+$: 351.9336, found 351.9336.



(4-Chlorophenyl)tetrafluoro(trifluoromethyl)-λ⁶-tellane (Te-4b). The reaction was run according to the **general procedure L**. White solid; m.p. 45.2-47.8 °C. ^{19}F NMR (377 MHz, CD_3CN): -53.82 (3F, quint, J = 22.3 Hz), -67.67 (4F, q, J = 22.3 Hz); ^{1}H NMR (400 MHz, CD_3CN): 8.00 (2H, dm, J = 9.0 Hz), 7.82 (2H, dquint, J = 9.0, 1.2 Hz); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): 143.2, 140.6 (quint, J = 10.2 Hz), 132.72-132.64 (m), 132.70-132.62 (m), 129.88 (qquint, J = 357.3, 53.5 Hz). ν_{max} (ATR-IR): 617 cm^{-1} (br). HRMS (EI): calc'd for $C_7H_4F_7ClTe$ $[M]^+$: 385.8947, found 385.8945. Additionally, single crystals suitable for X-ray analysis were obtained by solvent evaporation at rt under inert atmosphere using MeCN.

6.3.5 Procedures and Results Regarding Reactivity of **Te-2a**

General Procedure for Reaction Attempts with Alkene or Alkyne Substrates

An oven-dried microwave vial equipped with stir bar was charged with $PhTeF_5$ (30 mg, 0.1 mmol, 1.0 eq.), the substrate (0.1 mmol, 1.0 eq.), and 1.2 mL anhydrous DCM. The vial was sealed with a cap with a septum, and the reaction mixture was stirred under the specified conditions in the appendix. At the specified time, an aliquot was taken for ^{19}F NMR analysis. See the appendix for details.

General Procedure for Reaction Attempts with Nucleophile Substrates

An oven-dried microwave vial equipped with stir bar was charged with $PhTeF_5$ (15 mg, 0.05 mmol, 1.0 eq.), the substrate (0.05 mmol, 1.0 eq.), and 1.2 mL anhydrous solvent. The vial was sealed with a cap with a septum, and the reaction mixture was stirred under the specified conditions in Table S3. At the specified time, an aliquot was taken for ^{19}F NMR analysis. See the appendix for details.

General Procedure for Reaction Attempts with TMS-based Substrates

An oven-dried microwave vial equipped with stir bar was charged with $PhTeF_5$ (30 mg, 0.1 mmol, 1.0 eq.), the substrate (0.1 mmol, 1.0 eq.), and 1.2 mL anhydrous MeCN. *Note that some reactions were also carried out in the presence of CsF (15 mg, 0.1 mmol, 1.0 eq.).* The vial was sealed with a cap with a septum, and the reaction mixture was stirred under the specified conditions in Table S3. At the specified time, an aliquot was taken for ^{19}F NMR analysis. See the appendix for details.

General Procedure for Photochemical Reaction Attempts with/without Photosensitizers

An oven-dried microwave vial equipped with stir bar was charged with $PhTeF_5$ (15 mg, 0.05 mmol, 1.0 eq.), the substrate (0.05 mmol, 1.0 eq.), and 1.2 mL anhydrous MeCN. *Note that some reactions were also carried out in the presence of a photosensitizer (0.005 mmol, 0.1 eq.).* The vial was sealed with a cap with a septum, placed in a beaker wrapped with aluminum foil, and then the reaction mixture was stirred and irradiated at 300 nm using a pen lamp for 16 h. At the specified time, an aliquot was taken for ^{19}F NMR analysis. See the appendix for details.

Procedure for Hydrolysis of Pentafluoro(phenyl)-λ⁶-tellane (Te-2a)

A vial equipped with a stir bar was charged with $PhTeF_5$ (15 mg, 0.05 mmol, 1.0 eq.) and 2 mL 9:1 MeCN:H_2O. The reaction mixture was stirred open to air for 5 minutes. Subsequently, the contents of the vial were diluted with DCM and H_2O and transferred to

a separatory funnel. The reaction mixture was extracted into DCM, dried with $MgSO_4$, filtered through Celite, and concentrated. Virtually quantitative conversion to the corresponding *cis*-tetrafluoro(phenyl)-λ⁶-tellanol was determined by ^{19}F NMR. ^{19}F NMR (282 MHz, CD_3CN): -28.30 (1F, dt, J = 150.7, 127.1 Hz), -43.47 (1F, dt, J = 150.7, 111.0 Hz), -51.69 (2F, dd, J = 127.1, 111.0 Hz).

Procedure for Hydrolysis of Tetrafluoro(phenyl)(trifluoromethyl)-λ⁶-tellane (Te-4a)

A vial equipped with a stir bar was charged with $PhTeF_4CF_3$ (17 mg, 0.05 mmol, 1.0 eq.) and 2 mL 9:1 MeCN:H_2O. The reaction mixture was stirred open to air for 5 minutes. Subsequently, the contents of the vial were diluted with DCM and H_2O and transferred to a separatory funnel. The reaction mixture was extracted into DCM, dried with $MgSO_4$, filtered through Celite, and concentrated. Virtually quantitative conversion to the corresponding *eq*-trifluoro(phenyl)(trifluoromethyl)-λ⁶-tellanol was determined by ^{19}F NMR. ^{19}F NMR (282 MHz, CD_3CN): -49.99 (1F, tq, J = 59.4, 30.6 Hz)**,** -59.74 (3F, dt, J = 30.6, 19.8 Hz)**,** -73.24 (2F, dq, J = 59.4, 19.8 Hz). Note that a separate sample was dissolved in 9:1 CD_3CN:H_2O, and after 36 h, the putative dihydrolysis product difluoro(phenyl)(trifluoromethyl)-λ⁶-tellanediol was observed as the major product: ^{19}F NMR (282 MHz, CD_3CN): -59.97 (3F, t, J = 16.6 Hz), -72.16 (2F, q, J = 16.6 Hz).

Procedure for Reaction between Te-2a Generated in situ from Ph_2Te_2 and XeF_2 and Styrene

Diphenyl ditelluride (10 mg, 0.025 mmol, 1.0 equiv.) was dissolved in 0.5 mL CD_2Cl_2 in a PFA vessel equipped with a stir bar under N_2 atmosphere in a glove box. XeF_2 (21 mg, 0.125 mmol, 5.0 equiv.) was added in one portion, and a violent reaction occurred (with putative, rapid evolution of Xe gas out of solution). The reaction was stirred for an additional hour. At this point, styrene (0.05 mmol, 5.8 μl, 2.0 equiv.) was added to the PFA vessel, and the reaction mixture was stirred overnight. An aliquot was taken for ^{19}F NMR analysis with fluorobenzene as an internal standard.

Procedure for Reaction between XeF_2 and Styrene

Styrene (0.05 mmol, 5.8 μl, 1.0 equiv.) was dissolved in 0.5 mL CD_2Cl_2 in a PFA vessel equipped with a stir bar under N_2 atmosphere in a glove box. XeF_2 (8.5 mg, 0.05 mmol, 1.0 equiv.) was added in one portion, and the reaction mixture was stirred overnight. An aliquot was taken for ^{19}F NMR analysis with fluorobenzene as an internal standard.

Procedure for Reaction between Te-1a and Styrene in the Presence of Substoichiometric XeF_2

Pentafluoro(phenyl)-λ^6-tellane **1** (15 mg, 0.05 mmol, 1.0 equiv.) was dissolved in 0.5 mL CD_2Cl_2 in a PFA vessel equipped with a stir bar under N_2 atmosphere in a glove box. XeF_2 (2.5 mg, 0.015 mmol, 0.3 equiv.) was added in one portion, followed by styrene (0.05 mmol, 5.8 μl, 1.0 equiv.). The reaction mixture was stirred overnight. An aliquot was taken for ^{19}F NMR analysis with fluorobenzene as an internal standard. *Note that this reaction used **1** isolated from the TCICA/KF protocol.*

Procedure for Reaction between Te-2a and Styrene

Pentafluoro(phenyl)-λ^6-tellane **1** (15 mg, 0.05 mmol, 1.0 equiv.) was dissolved in 0.5 mL CD_2Cl_2 in a PFA vessel equipped with a stir bar under N_2 atmosphere in a glove box. Styrene (0.05 mmol, 5.8 μl, 1.0 equiv.) was then added, and the reaction mixture was stirred overnight. An aliquot was taken for ^{19}F NMR analysis with fluorobenzene as an internal standard. *Note that this reaction used **1** isolated from the TCICA/KF protocol.*

6.4 Experimental Details to Chapter 3

6.4.1 Procedures for Syntheses of Phosphine Starting Materials

Starting materials for **11**,[214] **15** – **18**[190] and **20** – **22**[190] and **24**,[215] were prepared according to literature. Triorganylphosphine oxides have been synthesized from their phosphine analogues according to literature.[185] $[SiEt_3(tol)][B(C_6F_5)_4]$ was prepared in dry toluene from trityl$[B(C_6F_5)_4]$ and $SiEt_3H$ as previously reported.[216]
The known compounds were not thoroughly analyzed and so their characterization data is not reported herein as they had been accessed and characterized by other groups before. Their purity was confirmed by ^1H and ^{31}P NMR. Starting materials for **1** – **10**, **12** – **14** and **19**, **28** are commercially available, and were used as received.

Procedure for the Synthesis of Compound P-1i

Into a flame-dried 50 ml two-necked round bottom flask, equipped with a reflux condenser, stir bar and septum, was given Ph_2PCl (1.10 g, 5 mmol, 1 equiv.), NaI (0.75 g, 5.0 mmol, 1 equiv.) and dry MeCN (10 mL) under an argon atmosphere. 1-Octanal (0.14 g, 1.1 mmol, 0.22 eq.) was injected into the flask by syringe. The reaction mixture was stirred at 80 °C for 24 h. The mixture was left to cool to rt and 30% H_2O_2 aqueous (0.5 ml) was added slowly by syringe. The mixture was stirred vigorously for 10 minutes and sat. aqueous $Na_2S_2O_3$ was added to the reaction mixture. The organic layer was extracted with DCM (3 x 20 ml), washed with brine (2 x 5 ml), dried over magnesium sulfate, filtered and concentrated *in vacuo*. The colorless solid was purified by flash column chromatography on silica gel (DCM:MeOH) to obtain the phosphine oxide.

Procedure for the Synthesis of Compounds P-1p – P-1w

Into a flame-dried 50 mL two-necked round bottom flask, equipped with a dropping funnel was added the corresponding Grignard reagent in THF or diethyl ether (10 mmol, 2 M, 3.3 equiv.) and the solution cooled to 0°C under an Ar atmosphere. A solution of diethylphosphite (0.39 ml, 3.0 mmol, 1.0 eq.) in THF (2 ml) was then added dropwise over 15 minutes. The mixture was stirred for 15 minutes at 0°C, allowed to warm to rt and stirred for two more hours. The mixture was cooled again to 0°C and HCl (0.1 M, 7.5 ml) was added added dropwise over 20 minutes. MTBE (30 ml) was added, and the mixture stirred vigorously for 5 min. The upper MTBE layer was separated by decantation and to the remaining gel was added DCM (20 ml). The mixture was again stirred vigorously for 5 minutes, filtered (celite) into a separatory funnel, and the filter cake washed with additional DCM (2 x 10 ml). The phases were separated and the organic phase combined with the first organic phase, dried with magnesium sulfate, and the concentrated *in vacuo*. The crude

mixtures were then purified by flash column chromatography (EtOAc:hexane) to afford the pure phosphine oxides.

Procedure for the Synthesis of P-1h

Into a flame-dried 50 mL two-necked round bottom flask, equipped with a dropping funnel was added 4-dimethylaminophenylmagnesium bromide solution in THF (10 mmol, 0.5 M, 3.3 equiv.) and the solution cooled to 0°C under an Ar atmosphere. The dropping funnel was charged with PCl_3 (0.42 g, 3 mmol, 1 equiv.) and diluted with THF (10 ml). The PCl_3 solution was then added dropwise to the stirred Grignard reagent. The mixture was stirred for 1 h at rt. The reaction was cooled to 0°C and quenched by slow addition of saturated aqueous NH_4Cl solution (50 ml) to the stirred suspension. The aqueous phase was extracted with $CHCl_3$ (3 x 50 ml), dried over magnesium sulfate and concentrated *in vacuo*. The product was oxidized according to the literature[185] and then purified by flash column chromatography (DCM:MeOH).

6.4.2 Procedure for the Synthesis of Triorganyldifluorophosphanes

General Procedure M for the Reaction of OPR_3 compounds with $(COCl)_2$/KF

Inside a glove box, spray-dried potassium fluoride (0.313 g, 5.40 mmol, 12.0 equiv.) was added to a polypropylene vial equipped with a stir bar. MeCN (4 mL) and a phosphine oxide (0.45 mmol, 1.0 equiv.) were added. Oxalyl chloride (0.12 mL, 1.35 mmol, 3.0 equiv.) was added in one portion while vigorously stirring the reaction mixture. Immediate gas evolution occurred upon addition of the oxalyl chloride. After ceasing of the gas evolution, the vial was sealed with a cap. The reaction mixture was stirred vigorously at room temperature overnight (ca. 16 h). Upon reaction completion, the reaction mixture was passed through a dry PTFE syringe filter, the solid residue was washed with additional dry MeCN (2 x 2 mL), and the volatiles of the filtrate were removed *in vacuo* to afford the corresponding crude difluorophosphanes. The crude was then washed with dry n-pentane (3 x 2 mL) and dried again *in vacuo* to afford the pure product.

Note: If impurities are still present in the product, it can be suspended in dry hexane:DCM (10:1, 3 x 5 mL), the suspension then filtered (PTFE syringe filter) and the solvent removed again *in vacuo*.

General Procedure N for the Reaction of $P(O)HR_2$ compounds with $(COCl)_2$/KF

Inside a glove box, spray-dried potassium fluoride (0.209 g, 3.60 mmol, 8.0 equiv.) was added to a polypropylene vial equipped with a stir bar. MeCN (4 mL) and oxalyl chloride (0.12 mL, 1.35 mmol, 3.0 equiv.) were added. The phosphine oxide (0.45 mmol, 1.0 equiv.) was added portion wise while vigorously stirring the reaction mixture. Immediate gas

evolution occurred upon addition of the phosphine oxide. After complete addition the vial was sealed with a cap. The reaction mixture was stirred vigorously at room temperature overnight (ca. 16 24 h). The purification procedure varies with the nature of the product (see below).
Note: In the case of more electron withdrawing phosphine oxides, the reaction time can exceed 16 h.

i) If the product is a **neutral** trifluorophosphane, upon reaction completion (clearly identifiable via ^{19}F or ^{31}P NMR), the reaction mixture is passed through a PTFE syringe filter, the solid residue is washed with additional MeCN (2 x 2 mL), and the volatiles of the filtrate are removed *in vacuo* to afford the corresponding trifluorophosphanes.
Note: If impurities are still present, the residue is suspended in a mixture of dry hexane:DCM (10:1, 3 x 3 mL), the suspension filtered and the volatiles are removed again *in vacuo* to afford the corresponding trifluorophosphanes.

ii) **Defluorination with TMSCl**
If the product was predominantly composed of the **anionic** phosphate (clearly identifiable via ^{19}F or ^{31}P NMR), the reaction mixture was passed through a PTFE syringe filter, the solid residue was washed with additional MeCN (2 x 2 mL), and the resulting filtrate was concentrated to dryness *in vacuo*. The solid crude was washed with Et_2O (3 x 5 mL), and dried again *in vacuo*. The solid was dissolved in dry MeCN (2 mL) and to it was given rigorously dried TMSCl (0.1 mL, 0.79 mmol, 1.7 equiv.). A colorless precipitate (KCl) formed immediately upon addition of TMSCl, the suspension was stirred for 1 h, then filtered through a PTFE syringe filter again and the solvent of the filtrate was removed *in vacuo* to afford the desired trifluorophosphanes.

General Procedure O for the Reaction of $RPCl_2$, RP(O)H(OEt) and Lawesson's Reagent with $(COCl)_2$/KF
Inside a glove box, spray-dried potassium fluoride (0.627 g, 10.8 mmol, 24.0 equiv.) was added to a polypropylene vial equipped with a stir bar. MeCN (6 mL) and oxalyl chloride (0.3 mL, 3.38 mmol, 7.5 equiv.) were added. The phosphorus starting material (0.45 mmol, 1.0 equiv.) was added portion wise while vigorously stirring the reaction mixture. After complete addition the vial was sealed with a cap. The reaction mixture was stirred vigorously at room temperature overnight (ca. 16 h). The reaction mixture was passed through a PTFE syringe filter, the solid residue was washed with additional MeCN (2 x 2 mL), and the volatiles of the filtrate were removed *in vacuo*. The resulting solid residue was

washed with Et_2O (3 x 5 mL) to afford **29** as a potassium salt. The neutral $PhPF_4$ can be obtained following the defluorination procedure with TMSCl described above.

General Procedure P for the Reaction of R_2PF_3 Compounds with Silylium Ions

A solution of the phosphane (0.1 mmol) in 2 mL of toluene was added in one portion to a stirred emulsion of $[Et_3Si(tol)_2][B(C_6F_5)_4]$ (88 mg, 0.09 mmol) in 3 mL of toluene in a polypropylene vial. The emulsion changes color immediately (from dark brown to a lighter orange) and is stirred for 60 min. The solution was then left to separate into two layers, the top layer was decanted and the bottom layer is washed with toluene (3 x 3 mL). The resulting oil was washed with n-pentane (3 x 2 ml) and the solid dried *in vacuo* to afford a spongy off-white solid.

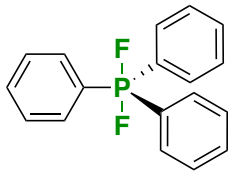
Procedure for the Reaction of $P(O)H(OEt)_2$ with $(COCl)_2$/KF

Inside a glove box, spray-dried potassium fluoride (0.627 g, 10.8 mmol, 24.0 equiv.) was added to a polypropylene vial equipped with a stir bar. MeCN (6 mL) and oxalyl chloride (0.6 mL, 6.77 mmol, 15.0 equiv.) were added. Diethyl phosphite (0.62 g, 0.45 mmol, 1.0 equiv.) was added at once while vigorously stirring the reaction mixture leading to immediate gas formation. After complete addition the vial was sealed with a cap and the reaction mixture was stirred vigorously at room temperature overnight (ca. 24 h). The reaction mixture was passed through a PTFE syringe filter, the solid residue is washed with additional MeCN (2 x 2 mL), and the volatiles of the filtrate are removed *in vacuo*. The resulting brown solid residue was washed with Et_2O (3 x 5 mL), dissolved in H_2O (1 ml) and a saturated solution of TBACl (1 ml) was added. A white precipitate formed, was filtered off, and washed with additional H_2O (3 x 1 mL) to afford **40** as an off-white solid.

Procedure for the Synthesis of As-1a and Sb-1a

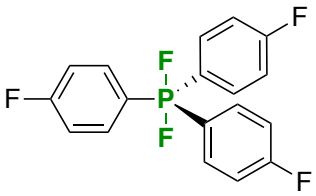
The reactions are carried out analogously to general procedure M. Purification of **Sb-1a** is achieved by column chromatography on silica gel eluting with n-hexane.

6.4.3 Analytical Data of R_3PF_2 Compounds



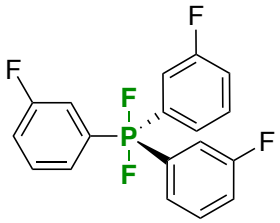
Difluorotriphenyl-λ⁵-phosphane (P-2a). The reaction was run according to the general procedure M, and the product is consistent with previously reported characterization data. Colorless solid.

^{1}H NMR (500 MHz, MeCN-d_3): 7.98 (6H, ddd, J = 15.3, 8.5, 1.4 Hz), 7.60 – 7.56 (3H, m), 7.55 – 7.46 (6H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -38.10 (2F, d, J = 655.6 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -53.6 (1P, t, J = 655.6 Hz); ^{13}C{^{1}H} NMR (125 MHz, MeCN-d_3) 137.4 (dt, J = 180.8, 29.2 Hz), 134.4 (dt, J = 12.9, 8.9 Hz), 132.7 (dt, J = 3.8, 1.3 Hz), 129.6 (dt, J = 16.7, 1.5 Hz). HRMS (EI): calc'd for $C_{18}H_{15}F_2P$ $[M]^+$: 300.0879, found: 300.0876.



Difluorotris(4-fluorophenyl)-λ⁵-phosphane (P-2b). The reaction was run according to the general procedure M, and the product is consistent with previously reported characterization data. Colorless solid.

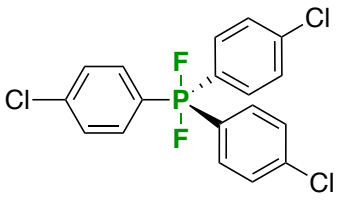
^{1}H NMR (300 MHz, MeCN-d_3): 8.04 (6H, ddd, J = 14.5, 8.9, 5.7 Hz), 7.23 (6H, td, J = 8.9, 3.5 Hz); ^{19}F NMR (282 MHz, MeCN-d_3): -38.33 (2F, d, J = 666.6 Hz), -109.14 (3F, s); ^{31}P NMR (121 MHz, MeCN-d_3): -58.3 (1P, t, J = 666.6 Hz).



Difluorotris(3-fluorophenyl)-λ⁵-phosphane (P-2f). The reaction was run according to the general procedure M. Colorless solid.

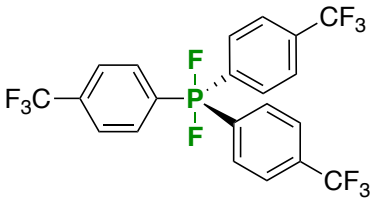
^{1}H NMR (400 MHz, MeCN-d_3): 7.83 (3H, dd, J = 14.8, 7.9 Hz), 7.74 (3H, ddt, J = 16.7, 10.1, 2.2 Hz), 7.53 (3H, ddd, J = 13.8, 8.1, 5.7 Hz), 7.34 (3H, td, J = 8.4, 2.8 Hz); ^{19}F NMR (376 MHz, MeCN-d_3): -37.79 (2F, d, J = 680.2 Hz), -113.37 – -113.73 (3F, m); ^{31}P NMR (161 MHz, MeCN-d_3): -58.3 (1P, t, J = 680.2 Hz); ^{13}C{^{1}H} NMR (101 MHz, MeCN-d_3):

163.5 (ddt, J = 245.8, 24.3, 1.8 Hz) 131.7 (ddt, J = 19.9, 7.7, 1.8 Hz) 130.8 (dtd, J = 12.5, 9.5, 3.1 Hz) 121.5 (ddt, J = 24.0, 14.4, 9.7 Hz) 120.1 (dd, J = 21.2, 3.6 Hz).



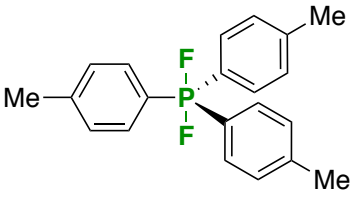
Difluorotris(4-chlorophenyl)-λ⁵-phosphane (P-2c). The reaction was run according to the general procedure M. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): 7.95 (6H, dd, J = 14.8, 8.7 Hz), 7.51 (6H, dd, J = 8.7, 3.8 Hz); ^{19}F NMR (282 MHz, MeCN-d_3): -44.87 (2F, d, J = 669.6 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -57.0 (1P, t, J = 669.6 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 144.3 (s), 139.2 – 138.9 (m), 136.5 (dt, J = 14.4, 9.4 Hz); 135.3 (dt, J = 186.0, 30.0 Hz), 129.8 (d, J = 17.9 Hz).



Difluorotris(4-(trifluoromethyl)phenyl)-λ⁵-phosphane (P-2d). The reaction was run according to the general procedure M, and the product is consistent with previously reported characterization data. Colorless solid.

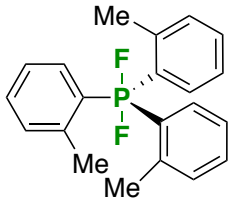
^{1}H NMR (300 MHz, MeCN-d_3): 8.16 (6H, dd, J = 15.2, 8.1 Hz), 7.83 (6H, dd, J = 8.4, 4.1 Hz); ^{19}F NMR (282 MHz, MeCN-d_3): -36.44 (2F, d, J = 676.5 Hz), -63.51 (12F, s); ^{31}P NMR (121 MHz, MeCN-d_3): -55.4 (1P, t, J = 676.5 Hz).



Difluorotri-p-tolyl-λ⁵-phosphane (P-2n). The reaction was run according to the general procedure M. Colorless solid.

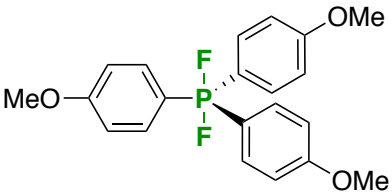
^{1}H NMR (300 MHz, MeCN-d_3): 7.85 (6H, dd, J = 14.9, 8.3 Hz), 7.29 (6H, dd, J = 8.1, 4.5 Hz), 2.37 (9H, s); ^{19}F NMR (282 MHz, MeCN-d_3): -39.83 (2F, d, J = 651.5 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -55.52 (1P, t, J = 651.5 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3):

143.1 (s), 134.5 (dt, J = 13.3, 8.9 Hz), 134.4 (dt, J = 183.7, 29.9 Hz), 130.2 (d, J = 17.0 Hz), 21.4 (d, J = 1.8 Hz).



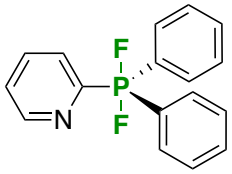
Difluorotri-o-tolyl-λ⁵-phosphane (P-2m). The reaction was run according to the general procedure M and the product is consistent with previously reported characterization data.[217] Colorless solid. Obtained as a mixture of fluorophosphonium fluoride and difluorophosphane.

^{1}H NMR (400 MHz, MeCN-d_3): Mixture: 7.95 (t, J = 7.9 Hz), 7.72 (t, J = 6.8 Hz), 7.58 (d, J = 7.8 Hz), 7.53 (d, J = 7.9 Hz), 7.44 (t, J = 7.6 Hz), 7.34-7.27 (m), 2.44 (s), 2.24(s); ^{19}F NMR (376 MHz, MeCN-d_3): Phosphonium Fluoride: -125.89 (2F, d, J = 987.5 Hz); Difluorophosphane: -25.37 (2F, d, J = 624.1 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): Phosphonium Fluoride: 103.01 (1P, d, J = 987.5 Hz); Difluorophosphane: -34.97 (1P, t, J = 624.1 Hz); Ratio difluorophosphane:phosphonium Fluoride by ^{19}F NMR = 4.6:1.



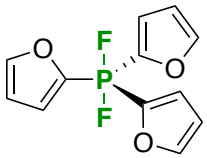
Difluorotris(4-methoxyphenyl)-λ⁵-phosphane (P-2e). The reaction was run according to the general procedure M. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): 7.93 (6H, m), 7.00 (6H, m), 3.83 (9H, s); ^{19}F NMR (282 MHz, MeCN-d_3): -42.36 (2F, d, J = 651.4 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -59.4 (1P, t, J = 651.4 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 144.2 (dd, J = 365.6, 106.7 Hz), 136.6 (dt, J = 14.7, 9.9 Hz), 128.8 (dt, J = 189. 7, 30.1 Hz),114.7 (d, J = 17.7 Hz), 56.0 (s).



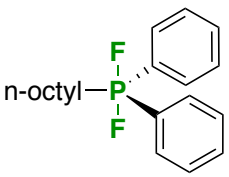
2-(Difluorodiphenyl-λ⁵-phosphaneyl)pyridine (P-2k). The reaction was run according to the general procedure M, and the product is consistent with previously reported characterization data. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): 8.77 (1H, d, J = 4.9 Hz), 8.14 (4H, dd, J = 15.0, 7.0 Hz), 7.99 (1H, q, J = 7.1 Hz), 7.89 (1H, t, J = 7.9 Hz), 7.68 – 7.39 (7H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -40.16 (2F, d, J = 676.0Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -57.5 (1P, t, J = 676.0 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 160.8 (s), 149.3 (d, J = 23.4 Hz), 139.8 (d, J = 13.3 Hz),135.6 (dt, J = 13.0, 9.7 Hz), 135.0 (dt, J = 179.2, 27.1 Hz), 133.4 (d, J = 3.9 Hz), 129.7 (dt, 16.7, 1.7 Hz), 128.3 (dt, J = 28.5, 5.7 Hz), 127.0 (d, 4.1 Hz).



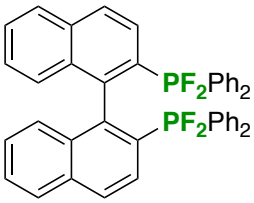
Difluorotri(furan-2-yl)-λ^5-phosphane (P-2l). The reaction was run according to the general procedure M, and the product is consistent with previously reported characterization data. Colorless solid.

^{1}H NMR (400 MHz, MeCN-d_3): 7.85 (3H, br s), 7.41 (3H, br s), 6.61 (3H, br s); ^{19}F NMR (376 MHz, MeCN-d_3): -63.66 (2F, d, J = 675.0 Hz); ^{31}P (161 MHz, MeCN-d_3): -89.85 (1P, t, J = 675.0 Hz); ^{13}C{^{1}H} NMR (101 MHZ, MeCN-d_3): 150.6 (d, J = 11.8 Hz), 145.6 (dt, J = 263.9, 43.5 Hz), 128.1 (dt, J = 29.6, 6.6 Hz), 113.0 (dt, J = 12.6, 2.1 Hz).



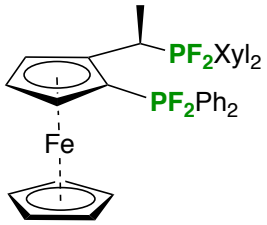
Difluoro(octyl)diphenyl-λ^5-phosphane (P-2i). The reaction was run according to the general procedure M. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): 8.01 (4H, ddd, J = 14.7, 8.0, 1.7 Hz) 7.60 – 7.36 (6H, m), 2.44 (2H, ddt, J = 20.6, 16.7, 8.2 Hz), 1.89 – 1.68 (2H, m), 1.46 – 1.16 (10H, m), 0.90 (3H, t, J = 6.6 Hz); ^{19}F NMR (282 MHz, MeCN-d_3): -39.39 (dt, J = 638.8, 12.2 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -41.76 (t, J = 638.8 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 136.3 (dt, J = 172.5, 27.3 Hz), 134.1 (dt, J = 12.6, 9.3 Hz), 131.4 (d, J = 3.7 Hz), 128.4 (d, J = 16.1 Hz), 36.3 (dt, J = 129.4, 28.7 Hz), 31.9 (s), 31.1 (d, J = 21.3 Hz), 29.30 (d, J = 1.3 Hz), 29.27 (s), 24.1 (d, J = 5.0 Hz), 22.8 (s), 14.2 (s).



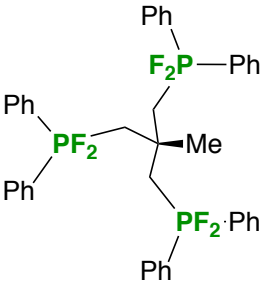
2,2'-Bis(difluorodiphenyl-λ⁵-phosphaneyl)-1,1'-binaphthalene (P-2j). The reaction was run according to the general procedure M. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): 7.97 – 7.01 (12H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -35.79 (2F, d, J = 685.4 Hz); ^{31}P (121 MHz, MeCN-d_3): -52.6 (1P, t, J = 685.4 Hz); ^{13}C{^{1}H} NMR (125 MHz, MeCN-d_3): 140.4 (dt, J = 195.8, 34.7 Hz), 136.1 (q, J = 11.2 Hz), 136.0 (dt, J = 177.6, 26.2 Hz), 134.7 (d, J = 17.3 Hz), 133.9 (d, J = 3.0 Hz), 132.2 (d, J = 3.6 Hz), 129.24-128.69 (m), 128.5 (s), 127.5 (s), 127.1 (s), 127.0 (s).



Compound 13, tetrafluoro-Xyliphos (P-2o). The reaction was run according to the general procedure M. Dark brown solid.

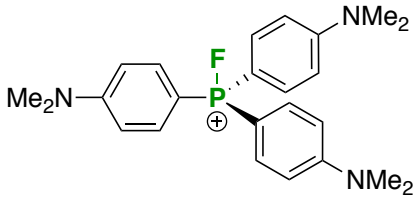
^{1}H NMR (400 MHz, MeCN-d_3): 7.80 (4H, dd, J =14.8, 7.6 Hz), 7.47-7.37 (6H, m), 7.19 (4H, d, J = 14.1), 6.99 (2H, s), 4.88 (1H, s), 4.67 (1H, s), 4.55 (1H, s), 3.94 (5H, s), 2.19 (12H, br s), 1.76 (3H, dd, J = 2.4, 7.2 Hz); ^{19}F NMR (376 MHz, MeCN-d_3): -34.5 (2F, d, J = 673.7 Hz), -46.02 (2F, dd, J = 694.9, 12.35 Hz); ^{31}P NMR (161 MHz, MeCN-d_3): -46.35 (1P, t, J = 694.9 Hz), -52.08 (1P, t, J = 673.7 Hz). ^{13}C{^{1}H} NMR: The compound decomposes in solution over time, thus no conclusive ^{13}C NMR could be measured.



(2-((Difluorodiphenyl-λ⁵-phosphaneyl)methyl)-2-methylpropane-1,3-diyl)bis(difluorodiphenyl-λ⁵-phosphane) (P-2g). The reaction was run according to the general procedure M. Colorless solid.

^{1}H NMR (400 MHz, MeCN-d_3): 7.79 (12H, dd, J = 14.62, 7.25 Hz), 7.55 – 7.51 (6H, m), 7.43 (12H, dd, J = 7.63, 4.72 Hz), 2.93 (6H, d, J = 17.53 Hz), 1.27 (3H, s); ^{19}F NMR (376

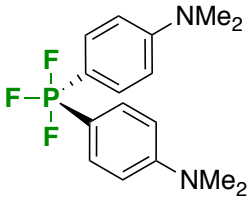
MHz, MeCN-d_3): -33.67 (6F, d, J = 651.2 Hz); ^{31}P NMR (161 MHz, MeCN-d_3): -43.7 (3P, t, J = 651.2 Hz); ^{13}C{^{1}H} NMR (101 MHz, MeCN-d_3): 158.6 (d, J = 95.9 Hz), 146.0 (d, J = 371.1 Hz), 144.4 (dd, J = 365.8, 106.7 Hz); 134.9 (d, J = 12.9 Hz), 132.7 (d, J = 3.6 Hz), 129.6 (d, J = 16.1 Hz).



Tris(4-(dimethylamino)phenyl)fluorophosphonium (P-2h). The reaction was run according to the general procedure M. Off-white solid.

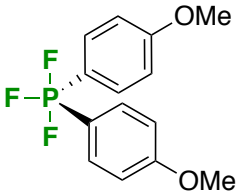
^{1}H NMR (400 MHz, MeCN-d_3): 7.47 (6H, dd, J = 12.6, 9.1 Hz), 7.00 (6H, dd, J = 9.1, 3.2 Hz), 3.10 (18H, s); ^{19}F NMR (376 MHz, MeCN-d_3): -109.94 (1F, d, J = 971.9 Hz); ^{31}P NMR (161 MHz, MeCN-d_3): 90.0 (1P, d, J = 971.9 Hz); ^{13}C{^{1}H} NMR (101 MHz, MeCN-d_3): 156.1 (d, J = 2.4 Hz), 136.2 (d, J = 14.1 Hz), 113.0 (d, J = 15.0 Hz), 101.6 (dd, J = 128.8, 21.0 Hz), 40.3 (s).

6.4.4 Analytical Data of R_2PF_3 Compounds and Salts Thereof



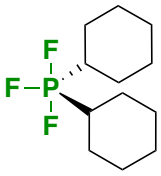
Trifluorobis(4-dimethylaminophenyl)-λ⁵-phosphane (P-3e). The reaction was run according to the general procedure N. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): 7.80 (4H, dd, J = 13.6, 9.2 Hz), 6.66 (4H, dd, J = 9.2, 4.6 Hz), 2.93 (12H, s); ^{19}F NMR (282 MHz, MeCN-d_3): -44.77 (2F, dd, J = 813.0, 35.8 Hz), -77.77 (1F, dt, J = 946.5, 35.9 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -38.3 (1P, dt, J = 946.5, 813.0 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 136.17 (d, J = 14.1 Hz), 112.95 (d, J = 15.0 Hz), 101.57 (dd, J = 128.8, 21.0 Hz), 40.30 (s).



Trifluorobis(4-methoxyphenyl)-λ⁵-phosphane (P-3f). The reaction was run according to the general procedure N. Colorless oil.

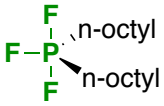
^{1}H NMR (300 MHz, MeCN-d_3): 8.05 (4H, dd, J = 14.27, 9.06 Hz), 7.06 (4H, dd, 9.06, 4.58 Hz) 3.86 (6H, s); ^{19}F NMR (282 MHz, MeCN-d_3): -38.76 (2F, dd, J = 823.61, 35.89 Hz), -78.70 (1F, dt, J = 953.64, 35.84 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -36.8 (1P, dtdtdt, J = 953.6, 823.8, 19.0, 14.3, 9.6, 4.6 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 164.8 (d, J = 4.1 Hz), 138.5 (dt, J = 15.6, 11.2 Hz), 124.3 (dtd, J = 222.2, 32.7, 9.4 Hz); 115.3 (dt, J = 18.8, 2.0 Hz).



Trifluorodicyclohexyl-λ⁵-phosphane (P-3g). The reaction was run according to the general procedure N, and the product is consistent with previously reported characterization data. Colorless oil.

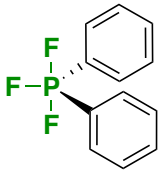
^{1}H NMR (300 MHz, MeCN-d_3): 2.16 (1H, J = 11.88, 2.87), 2.05 – 2.00 (2H, m) 1.83 – 1.79 (2H, m), 1.72 – 1.70 (1H, m), 1.52 – 1.45 (2H, m), 1.38 – 1.26 (3H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -41.82 (2F, ddt, J = 842.32, 27.44, 12.27 Hz), -96.42 (1F, dt, J = 978.27, 27.44

Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -52.6 (1P, t, J = 685.35 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 44.7 (dtd, J = 134.1, 24.1, 4.3 Hz), 27.5 (q, J = 4.7 Hz), 26.9 (d, J = 18.9 Hz); 26.8 (d, J = 2.2 Hz).



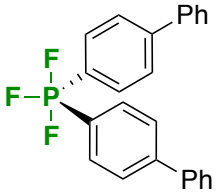
Trifluorodioctyl-λ^5-phosphane (P-3h). The reaction was run according to the general procedure N. Colorless oil.

^{1}H NMR (300 MHz, MeCN-d_3): 2.10 (4H, tdd, J = 16.4, 11.7, 8.2 Hz), 1.64 (4H, tt, 15.1, 7.5 Hz), 1.42 – 1.22 (20H, m), 0.97 – 0.84 (6H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -23.74 (2F, ddp, J = 810.7, 28.1, 11.7 Hz), -91.46 (1F, dtt, J = 975.7, 28.1, 3.3 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): 7.7 (1P, dtdp, J = 975.7, 810.7, 29.8, 14.9 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 34.9 (dtd, J = 139.4, 27.2, 5.0 Hz), 32.6 (s), 31.2 (dd, J = 19.4, 2.6 Hz); 29.4 (s), 28.2 (d, J = 87.4, 14.8 Hz), 23.52 (q, J = 5.5 Hz), 23.4 (s), 14.4 (s).



Trifluorodiphenyl-λ^5-phosphane (P-3a). The reaction was run according to the general procedure N, and the product is consistent with previously reported characterization data. Colorless oil.

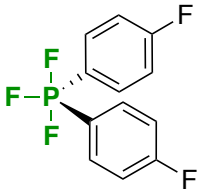
^{1}H NMR (300 MHz, $CDCl_3$): 8.09 (6H, ddd, J = 15.4, 8.5, 1.4 Hz), 7.60 (3H, td, J = 7.1, 1.6 Hz), 7.50 (6H, q, J = 7.5 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): -35.35 (2F, dd, J = 836.9, 38.4 Hz), -80.20 (1F, dt, J = 972.2, 38.5 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): -34.37 (1P, dt, J = 972.2, 836.9 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 135.11 (dt, J = 13.6, 10.1 Hz), 133.75-132.91 (m), 132.97 (dtd, J = 207.7, 32.0, 8.1 Hz), 128.74 (dt, J = 17.9, 1.8 Hz).



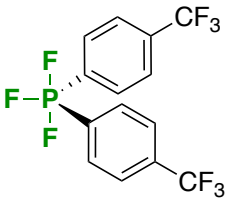
Di([1,1'-biphenyl]-4-yl)trifluoro-λ^5-phosphane (P-3b). The reaction was run according to the general procedure N. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): 8.06 (4H, dd, J = 15.5, 8.4 Hz), 7.76–7.48 (14H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -35.43 (2F, dd, J = 833.8, 36.2 Hz), -82.18(1F, dtt, J = 964.3 36.3 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -33.01 (1P, dt, J = 964.3, 833.8 Hz); ^{13}C{^{1}H}

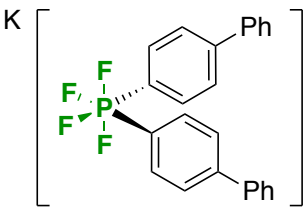
NMR (75 MHz, MeCN-d_3): 135.2 (dtd, *J* = 135.3, 13.6, 9,8 Hz), 135.4 (dt, *J* = 13.8, 9.8), 134.7 – 134.6 (m), 133.7 (s), 130.2 (s), 129.9 (dt, *J* = 17.9, 1.9 Hz).



Trifluorobis(4-fluorophenyl)-λ⁵-phosphane (P-3c). The reaction was run according to the general procedure N. Colorless oil.
^{1}H NMR (300 MHz, $CDCl_3$): 8.05 (6H, ddd, *J* = 14.6, 8.9, 5.6 Hz), 7.11 (6H, td, *J* = 8.6, 4.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): -35.61 (2F, dd, *J* = 835.8, 39.0 Hz), -79.20 (dt, *J* = 970.3, 38.9 Hz), -104.33 (2F, m); ^{31}P NMR (121 MHz, $CDCl_3$): -37.76 (1P, dt, *J* = 970.3, 835.8 Hz); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): 166.2 (dd, *J* = 256.2, 4.4 Hz), 138.4 (dtd, *J* = 15.7, 10.9, 9.2 Hz), 128.4 (dtdd, *J* = 219.1, 33.3, 8.9, 3.3 Hz), 116.2 (ddt, *J* = 21.5, 19.6, 1.9 Hz).

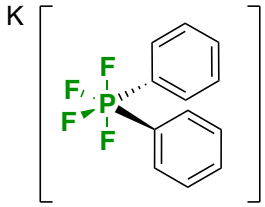


Trifluorobis(4-(trifluoromethyl)phenyl)-λ⁵-phosphane (P-3d). The reaction was run according to the general procedure N. Colorless oil.
^{1}H NMR (300 MHz, MeCN-d_3): 8.05 (4H, dd, *J* = 15.43, 8.10 Hz), 7.06 (4H, dd, 8.37, 5.03 Hz); ^{19}F NMR (282 MHz, MeCN-d_3): -30.70 (2F, dd, *J* = 843.65, 38.42 Hz), -63.77 (6F, s), -80.86 (1F, dt, *J* = 974.49, 38.44 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -34.2 (1P, dt, *J* = 973.8, 843.9 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 137.0 (dtd, *J* = 212.6, 32.7 8.2 Hz), 136.2 (dt, *J* = 14.5, 9.6 Hz) 135.5 (dq, *J* = 32.7, 4.0 Hz), 127.2-126.3 (m), 124.6 (q, *J* = 273.1, 272.6 Hz).

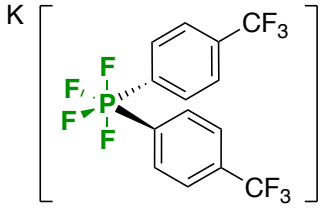


Potassium di([1,1'-biphenyl]-4-yl)tetrafluorophosphate (cis- and trans-P-4b). The reaction was run according to the general procedure N. Colorless solid as a mixture of isomers.

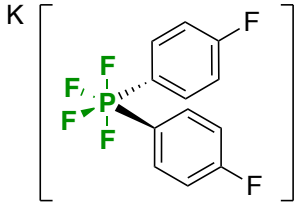
^{1}H NMR (300 MHz, MeCN-d_3): mixture: 7.82 (2H, dd, *J* = 17.4, 8.3 Hz), 7.72-7.39 (14H, m), 7.32 (2H, q, *J* = 7.5 Hz); ^{19}F NMR (282 MHz, MeCN-d_3): *cis*: -41.48 (2F, dt, *J* = 719.9, 36.8 Hz), -67.62 (2F, dt, *J* = 783.3, 36.8 Hz); *trans*: -45.04 (4F, d, *J* = 871.2 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): *trans*: -133.54 (1P, p, *J* = 871.2 Hz); *cis*: -125.8-150.5 (1P, m). Ratio *cis*:*trans* = 1.44:1.



Potassium tetrafluorodiphenyl-λ^6-phosphate (cis- and trans-P-4a). The reaction was run according to the general procedure N. Colorless solid as a mixture of isomers.
^{1}H NMR (300 MHz, MeCN-d_3): mixture: 7.75 (dd, *J* = 17.9, 7.7 Hz) 7.49 (dd, *J* = 13.6, 7.3 Hz) 7.33-6.90 (m); ^{19}F NMR (282 MHz, MeCN-d_3): *cis*: -41.04 (2F, dt, *J* = 711.6, 36.7 Hz), -67.68 (2F, dt, *J* = 786.5, 36.8 Hz); *trans*: -45.43 (4F, d, *J* = 874.1 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): cis: -135.75 (1P, tt, *J* = 786.8, 711.2 Hz), trans: -129.26 (1P, p, *J* = 874.4 Hz). Ratio *cis*:*trans* = 1.38:1.



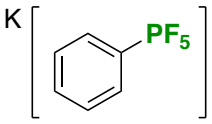
Potassium tetrafluorobis(4-(trifluoromethyl)phenyl)-λ^6-phosphate (cis- and trans-P-4d). The reaction was run according to the general procedure N. Colorless solid.
^{1}H NMR (300 MHz, MeCN-d_3): *cis*: 7.61 (dd, *J* = 12.9, 8.1 Hz), 7.43 (dd, *J* = 8.3, 3.5 Hz); *trans*: 7.89 (dd, *J* = 17.2, 8.0 Hz), 7.52 (dd, *J* = 7.6, 4.9 Hz); ^{19}F NMR (282 MHz, MeCN-d_3): *cis*: -43.58 (2F, dt, *J* = 730.3, 36.3 Hz), -62.11 (6F, s), -67.56 (2F, dt, *J* = 781.3, 36.2 Hz); *trans*: -45.45 (4F, d, *J* = 868.8 Hz), -61.93 (6F, s); ^{31}P NMR (121 MHz, MeCN-d_3): *cis*: -144.1 (1P, tt, *J* = 781.1, 729.3 Hz); *trans*: -135.8 (1P, p, *J* = 867.6 Hz). Ratio cis:trans = 1:1.59.



Potassium tetrafluorobis(4-fluorophenyl)-λ⁶-phosphate (cis- and trans-P-4c). The reaction was run according to the general procedure N. Colorless solid as a mixture of isomers.

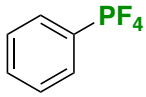
^{1}H NMR (300 MHz, MeCN-d_3): mixture: 7.70 (4H, ddd, J = 17.3, 8.8, 6.3 Hz), 7.44 (4H, ddd, J = 12.8, 8.7, 6.3 Hz), 6.92 (4H, td, J = 9.0, 4.0 Hz), 6.85 (4H, td, J = 9.2, 3.0 Hz); ^{19}F NMR (282 MHz, MeCN-d_3): *cis*: -41.58 (2F, dt, J = 719.9, 36.6 Hz), -65.90 (2F, dt, J = 781.0, 36.5 Hz), -119.96 (2F, m); *trans*: -43.99 (4F, d, J = 867.9 Hz), -119.17 (2F, m); ^{31}P NMR(121 MHz, MeCN-d_3): *trans*: -133.69 (1P, p, J = 867.9 Hz); *cis*: -138.03 (1P, tt, J = 781.6, 719.6 Hz). Ratio *cis*:*trans* = 1.0:1.0.

6.4.5 Analytical Data of RPF_4 Compounds and Salts Thereof



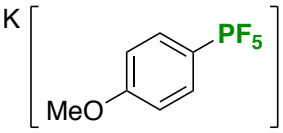
Potassium pentafloro(phenyl)-λ⁶-phosphate (P-5a). The reaction was run according to the general procedure O. The product is consistent with previously reported characterization data. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): 7.60 (2H, ddd, J = 16.2, 7.9, 1.8 Hz), 7.33-7.17 (3H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -58.36 (4F, dd, J = 823.3, 35.7 Hz), -60.76 (1F, dp, J = 526.5, 35.7 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -136.36 (1P, pd, J = 824.7, 668.6 Hz).



Tetrafluoro(phenyl)-λ⁵-phosphane (P-6a). The compound was accessed as described above and the product is consistent with previously reported characterization data. Colorless oil.

^{1}H NMR (300 MHz, MeCN-d_3): 8.15-7.79 (2H, m), 7.77-7.05 (2H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -54.36 (4F, d, J = 961.6 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): -49.75 (1P, p, J = 959.9 Hz); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 140.9 (d, J = 52.2 Hz), 134.1 (s), 130.9 (d, J = 31.6 Hz), 130.1 (d, J = 8.1 Hz).



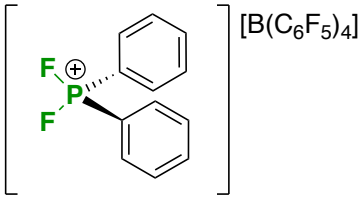
Potassium pentafluoro(4-methoxyphenyl)-λ⁶-phosphate (P-5b). The reaction was run according to the general procedure O. The product is consistent with previously reported characterization data. Colorless solid.

^{1}H NMR (300 MHz, MeCN-d_3): mixture: 7.49 (4H, dd, J = 15.5, 8.8 Hz), 6.76 (4H, dd, J = 8.4, 4.6 Hz), 3.75 (6H, s); ^{19}F NMR (282 MHz, MeCN-d_3): -57.55 (4F, dd, J = 818.6, 36.0 Hz), -60.84 (1F, dp, J = 676.2, 35.5 Hz); ^{31}P NMR (121 MHz, MeCN-d_3): trans: -136.9 (1P, pd, J = 818.6, 676.2 Hz).

$Bu_4N[PF_6]$

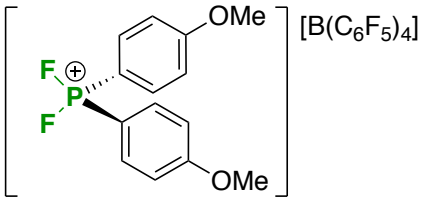
Tetrabutylammonium hexafluorophosphate (P-8a). The compound was prepared as described above. Off-white solid.

^{1}H NMR (300 MHz, $CDCl_3$): 3.15 (8H, br. s), 1.60 (8H, br. s), 1.41 (8H, q, J = 7.7, 7.2 Hz), 0.99 (12H, t, J = 6.9 Hz); ^{19}F NMR (282 MHz, $CDCl_3$): -72.24 (6F, d, J = 712.6 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): -144.35 (1P, sept, J = 712.6 Hz).



Difluorodiphenylphosphonium tetrakis(pentafluoro-phenyl) borate (P-7a). The reaction was run according to the general procedure P. Off-white solid.

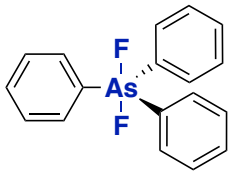
^{1}H NMR: 8.26 (2H, t, J = 7.8 Hz), 8.09 (4H, dd, J = 15.3, 7.8 Hz), 7.95 (4H, q, J = 7.5 Hz); ^{19}F NMR: -85.13 (2F, d, J = 1159.0 Hz), -133.11 (8F, m), -163.66 (4F, t, J = 20.4 Hz), -167.55 (8F, t, J = 19.1 Hz); ^{31}P NMR: 89.31 (1P, t, J = 1159.0 Hz); ^{11}B NMR: -16.68 (1B, s).



Difluorobis(4-methoxyphenyl)phosphonium tetrakis(pentafluoro-phenyl) borate (P-7b). The reaction was run according to the general procedure P. Off-white solid.

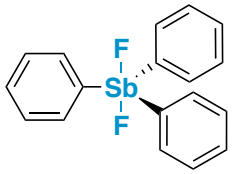
^{1}H NMR: 7.90 (4H, dd, J = 14.0, 8.7 Hz), 7.21 (4H, dd, J = 15.6, 7.8); ^{19}F NMR: -83.22 (2F, d, J = 1131.1 Hz), -133.11 (8F, m), -163.66 (4F, t, J = 20.4 Hz), -167.55 (8F, t, J = 19.1 Hz); ^{31}P NMR: 89.10 (1P, t, J = 1130.8 Hz); ^{11}B NMR: -16.83 (1B, s).

6.4.6 Analytical Data of Ph_3AsF_2 and Ph_3SbF_2



Difluorotriphenyl-λ⁵-arsane (As-1a). The reaction was run according to the procedure described above, and the product is consistent with previously reported characterization data.[218] Colorless solid. Yield: 77%.

^{1}H NMR (300 MHz, MeCN-d_3): 8.09 (6H, dd, J = 8.1, 1.7 Hz), 7.68-7.47 (9H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -89.82 (2F, s); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 138.2 (t, J = 18.6 Hz), 133.6 (t, J = 6.7 Hz), 133.1 (s), 130.2 (t, J = 1.2 Hz).



Difluorotriphenyl-λ⁵-stibane (Sb-1a). The reaction was run according to the procedure described above, and the product is consistent with previously reported characterization data.[192] Colorless solid. Yield: 58%.

^{1}H NMR (300 MHz, MeCN-d_3): 8.17 (6H, dd, J = 6.6, 3.0 Hz), 7.56 – 7.50 (9H, m); ^{19}F NMR (282 MHz, MeCN-d_3): -153.52 (2F, s); ^{13}C{^{1}H} NMR (75 MHz, MeCN-d_3): 135.5 (t, J = 4.9 Hz), 134.3 (t, J = 15.3 Hz), 132.3 (s), 129.7 (t, J = 1.6 Hz).

Bibliography

[1] A. Tressaud, in *Fluor. A Parad. Elem.*, **2019**, pp. 1–75.
[2] R. E. Banks, J. C. Tatlow, *J. Fluor. Chem.* **1986**, *33*, 227–346.
[3] N. Bartlett, *Proc. Chem. Soc.* **1962**, 197–236.
[4] A. Dickers, Die Spätmykenischen Siegel Aus Weichem Stein., VLM Verlag Marie Leidoerf GmbH, **2001**.
[5] J. R. Rumble, D. R. Lide, T. J. Bruno, *CRC Handbook of Chemistry and Physics*, CRC Press/Taylor & Francis, Boca Raton, FL, **2018**.
[6] A. R. Bliss Jr., *J. Am. Pharm. Assoc.* **1936**, *25*, 544–550.
[7] G. Agricola, *De Natura Fossilium*, Basel, **1546**.
[8] J. Schmedt auf der Günne, M. Mangstl, F. Kraus, *Angew. Chem.* **2012**, *124*, 7968–7971.
[9] H. Moissan, *C. R. Hebd. Seances Acad. Sci.* **1886**, *102*, 1543–1544.
[10] H. Groult, F. Lantelme, D. Devilliers, C. Belhomme, B. Morel, F. Nicolas, J.-P. Caire, *Actual. Chim.* **2006**, *38*, 40–46.
[11] H. Groult, F. Lantelme, M. Salanne, C. Simon, C. Belhomme, B. Morel, F. Nicolas, *J. Fluor. Chem.* **2007**, *128*, 285–295.
[12] R. D. Chambers, *Fluorine in Organic Chemistry*, Blackwell Publishing Ltd., Oxford, **2004**.
[13] T. Hiyama, *Organofluorine Compounds*, Springer, Berlin, Heidelberg, **2000**.
[14] P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley, **2004**.
[15] J.-P. Begue, D. Bonnet-Delpon, *Bioorganic and Medicinal Chemistry of Fluorine*, Hoboken, NJ, **2008**.
[16] I. Ojima, *Fluorine in Medicinal Chemistry and Chemical Biology*, Chichester, **2009**.
[17] A. Tressaud, *Fluorine, a Key Element for the 21st Century*, **2019**.
[18] A. F. Holleman, E. Wiberg, in *Lehrb. Der Anorg. Chemie*, De Gruyter, Berlin, New York, **2007**, pp. 498–650.
[19] Peter Haas, "Sulfur, S8, Cozzo Disi Mine, Sicily, Italy," can be found under https://www.mindat.org/, **2006**.
[20] G. Rapp, in *Archaeomineralogy*, Springer, Berlin, Heidelberg, **2009**, pp. 223–246.
[21] Homerus, *Odyssee*, Alphons Dürr, Leipzig, **1872**.
[22] A. K. Gupta, K. Nicol, *J. Drugs Dermatol.* **2004**, *3*, 427–431.
[23] W. H. Brock, B. Kleidt, H. Voelker, *Viewegs Geschichte Der Chemie*, Springer, Berlin, Heidelberg, **2012**.
[24] L. B. baron G. de Morveau, A. L. Lavoisier, C.-L. Berthollet, comte A.-F. de Fourcroy, J. H. Hassenfratz, P.-A. Adet, *Méthode de Nomenclature Chimique*, Chez Cuchet, **1787**.
[25] D. W. Thomson, *Eur. Hist. Q.* **1995**, *25*, 163–180.
[26] G. Kutney, *Sulfur : History, Technology, Applications & Industry*, Chem Tec Publishing,

Toronto, **2007**.
[27] B. Meyer, *Chem. Rev.* **1976**, *76*, 367–388. And references therein.
[28] H. Frasch, *Mining Sulfur*, **1891**, 461,429/31.
[29] C. F. Claus, *Obtaining Sulphur from Suplhide of Hydrogen*, **1882**, British Patent 3608.
[30] L. E. Apodaca, *Sulfur Statistics and Information*, **2020**.
[31] A. Togni, in *Molekül Der Woche Schwefelsäure*, Zürich, **2019**, p. 1.
[32] M.-T. Hao, C.-F. Du, C.-B. Tian, J.-R. Li, X.-Y. Huang, *Inorg. Chem. Commun.* **2016**, *72*, 128–131.
[33] J. A. Semlyen, *Trans. Faraday Soc.* **1967**, *63*, 2342–2345.
[34] K. Sugimoto, H. Uemachi, M. Maekawa, A. Fujiwara, *Cryst. Growth Des.* **2013**, *13*, 433–436.
[35] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Butterworth-Heinemann, Oxford, **1997**.
[36] M. Schmidt, H. Block, *Angew. Chem.* **1967**, *79*, 944.
[37] P. Liebing, M. Kühling, C. Swanson, M. Feneberg, L. Hilfert, R. Goldhahn, T. Chivers, F. T. Edelmann, *Chem. Commun.* **2019**, *55*, 14965–14967.
[38] G. Brauer, M. Baudler, in *Handb. Der Präparativen Anorg. Chemie*, Enke, Stuttgart, **1975**, pp. 183–184.
[39] C. Ni, M. Hu, J. Hu, *Chem. Rev.* **2015**, *115*, 765–825.
[40] H. Moissan, P. Lebeau, *C. R. Hebd. Seances Acad. Sci.* **1900**, *130*, 865.
[41] F. Nyman, H. L. Roberts, T. Seaton, J. W. George, *Inorg. Synth.* **1966**, 160–165.
[42] J. Wessel, G. Kleemann, K. Seppelt, *Chem. Ber.* **1983**, *116*, 2399–2407.
[43] R. Winter, R. J. Terjeson, G. L. Gard, *J. Fluor. Chem.* **1998**, *89*, 105–106.
[44] D. J. Burton, Y. Wang, in *Encycl. Reagents Org. Synth.*, Hoboken, NJ, **2004**, pp. 1–2.
[45] P. R. Savoie, J. T. Welch, *Chem. Rev.* **2015**, *115*, 1130–1190.
[46] J. T. Welch, D. S. Lim, *Bioorg. Med. Chem.* **2007**, *15*, 6659–6666.
[47] J. Fischer, W. Jaenckner, *Angew. Chem.* **1929**, *42*, 810–811.
[48] W. C. Smith, C. W. Tullock, E. L. Muetterties, W. R. Hasek, F. S. Fawcett, V. A. Engelhardt, D. D. Coffman, *J. Am. Chem. Soc.* **1959**, *81*, 3165–3166.
[49] W. C. Smith, *Angew. Chem. Int. Ed.* **1962**, *1*, 467–475.
[50] C.-L. J. Wang, *Org. React.* **2004**, 319–400.
[51] W. J. Middleton, *J. Org. Chem.* **1975**, *40*, 574–578.
[52] G. L. Lal, G. P. Pez, R. J. Pesaresi, F. M. Prozonic, H. Cheng, *J. Org. Chem.* **1999**, *64*, 7048–7054.
[53] J. Cochran, *Chem. Informationsd.* **1979**, *10*, 4.
[54] W. J. Middleton, *Chem. Informationsd.* **1979**, *10*, 43.
[55] M. Turcotte-Savard, O. Mahe, J. Paquin, *Chim. Oggi* **2013**, *31*, 14.

[56] T. Umemoto, R. P. Singh, Y. Xu, N. Saito, *J. Am. Chem. Soc.* **2010**, *132*, 18199–18205.
[57] F. Beaulieu, L.-P. Beauregard, G. Courchesne, M. Couturier, F. LaFlamme, A. L'Heureux, *Org. Lett.* **2009**, *11*, 5050–5053.
[58] K. A. Jolliffe, *Aust. J. Chem.* **2001**, *54*, 75.
[59] R. P. Singh, J. M. Shreeve, *Synthesis* **2002**, *2002*, 2561–2578.
[60] K. L. Kirk, *Org. Process Res. Dev.* **2008**, *12*, 305–321.
[61] D. O'Hagan, C. Schaffrath, S. L. Cobb, J. T. G. Hamilton, C. D. Murphy, *Nature* **2002**, *416*, 279.
[62] J. Charpentier, N. Früh, A. Togni, *Chem. Rev.* **2015**, *115*, 650–682.
[63] R. W. Steensma, S. Galabi, J. R. Tagat, S. W. McCombie, *Tetrahedron Lett.* **2001**, *42*, 2281.
[64] S. M. Shein, M. I. Krasnosel'skaya, V. N. Boiko, *Zh. Obs. Khim* **1966**, *36*, 2141–2147.
[65] M. D. Barrera, Y. Cheburkov, W. M. Lamanna, *J. Fluor. Chem.* **2002**, *117*, 13–16.
[66] G. K. S. Prakash, J. Hu, G. A. Olah, *Org. Lett.* **2003**, *5*, 3253–3256.
[67] J. Gong, P. L. Fuchs, *J. Am. Chem. Soc.* **1996**, *118*, 4486–4487.
[68] J. Gong, P. L. Fuchs, *Tetrahedron Lett.* **1997**, *38*, 787–790.
[69] J. Xiang, J. Evarts, A. Rivkin, D. P. Curran, P. L. Fuchs, *Tetrahedron Lett.* **1998**, *39*, 4163–4166.
[70] J. Xiang, W. Jiang, P. L. Fuchs, *Tetrahedron Lett.* **1997**, *38*, 6635–6638.
[71] N. V Kondratenko, O. A. Radchenko, L. M. Yagupol'skii, *Zh. Org. Khim.* **1984**, *16*, 2250.
[72] X. Shen, M. Zhou, C. Ni, W. Zhang, J. Hu, *Chem. Sci.* **2014**, *5*, 117.
[73] Y. Macé, C. Urban, C. Pradet, J. Marrot, J. C. Blazejewski, E. Magnier, *Eur. J. Org. Chem.* **2009**, 3150.
[74] S. Noritake, N. Shibata, S. Nakamura, T. Toru, M. Shiro, *Eur. J. Org. Chem.* **2008**, 3465.
[75] T. Umemoto, S. Ishihara, *J. Am. Chem. Soc.* **1993**, *115*, 2156–2164.
[76] C. Zhang, *Org. Biomol. Chem.* **2014**, *12*, 6580–6589.
[77] S. Altomonte, M. Zanda, *J. Fluor. Chem.* **2012**, *143*, 57–93.
[78] P. Kirsch, in *Mod. Fluoroorg. Chem.*, Wiley, Weinheim, **2004**, pp. 25–169.
[79] L. J. Sæthre, N. Berrah, J. D. Bozek, K. J. Børve, T. X. Carroll, E. Kukk, G. L. Gard, R. Winter, T. D. Thomas, *J. Am. Chem. Soc.* **2001**, *123*, 10729–10737.
[80] W. A. Sheppard, *J. Am. Chem. Soc.* **1962**, *84*, 3072.
[81] R. W. Taft, I. C. Lewis, *J. Am. Chem. Soc.* **1959**, *81*, 5343.
[82] R. W. Taft Jr, *J. Phys. Chem.* **1960**, *64*, 1805–1815.
[83] D. Lentz, K. Seppelt, K. Y. Akiba, *Chemistry of Hypervalent Compounds*, Wiley, New York, **1999**.

[84] M. Anthony, *Aust. N. Z. J. Med.* **1984**, *14*, 888–895.
[85] G. S. Dow, E. E. Milner, P. Wipf, T. Mo, *Derivatives of Mefloquine and Associated Methods for Making and Using*, **2010**, WO 2010/144434.
[86] P. J. Crowley, G. Mitchell, R. Salmon, P. A. Worthington, *Chimia (Aarau).* **2004**, *58*, 138–142.
[87] D. S. Lim, J. S. Choi, C. S. Pak, J. T. Welch, *J. Pestic. Sci.* **2007**, *32*, 255–259.
[88] G. A. Silvey, G. H. Cady, *J. Am. Chem. Soc.* **1950**, *72*, 3624–3626.
[89] W. A. Sheppard, *J. Am. Chem. Soc.* **1960**, *82*, 4751–4752.
[90] P. Kirsch, A. Hahn, *Eur. J. Org. Chem.* **2005**, *2005*, 3095–3100.
[91] A. M. Sipyagin, C. P. Bateman, Y.-T. Tan, J. S. Thrasher, *J. Fluor. Chem.* **2001**, *112*, 287–295.
[92] A. M. Sipyagin, V. S. Enshov, S. A. Kashtanov, C. P. Bateman, B. D. Mullen, Y.-T. Tan, J. S. Thrasher, *J. Fluor. Chem.* **2004**, *125*, 1305–1316.
[93] R. D. Bowden, P. J. Comina, M. P. Greenhall, B. M. Kariuki, A. Loveday, D. Philp, *Tetrahedron* **2000**, *56*, 3399–3408.
[94] X. Ou, A. F. Janzen, *J. Fluor. Chem.* **2000**, *101*, 279–283.
[95] T. Umemoto, L. M. Garrick, N. Saito, *Beilstein J. Org. Chem.* **2012**, *8*, 461–471.
[96] O. S. Kanishchev, W. R. Dolbier Jr., *Angew. Chem. Int. Ed.* **2015**, *54*, 280–284.
[97] B. Cui, M. Kosobokov, K. Matsuzaki, E. Tokunaga, N. Shibata, *Chem. Commun.* **2017**, *53*, 5997–6000.
[98] K. Lummer, M. V Ponomarenko, G.-V. Röschenthaler, M. Bremer, P. Beier, *J. Fluor. Chem.* **2014**, *157*, 79–83.
[99] L. Zhong, P. R. Savoie, A. S. Filatov, J. T. Welch, *Angew. Chem. Int. Ed.* **2014**, *53*, 526–529.
[100] V. Matoušek, E. Pietrasiak, R. Schwenk, A. Togni, *J. Org. Chem.* **2013**, *78*, 6763–6768.
[101] U. Tilstam, H. Weinmann, *Org. Process Res. Dev.* **2002**, *6*, 384–393.
[102] O. S. Kanishchev, W. R. Dolbier, *Org. Biomol. Chem.* **2018**, *16*, 5793–5799.
[103] H. Nakayama, J. Nishida, N. Takada, H. Sato, Y. Yamashita, *Chem. Mater.* **2012**, *24*, 671–676.
[104] P. Das, M. Takada, E. Tokunaga, N. Saito, N. Shibata, *Org. Chem. Front.* **2018**, *5*, 719–724.
[105] S. A. Lermontov, S. I. Zavorin, I. V Bakhtin, A. N. Pushin, N. S. Zefirov, P. J. Stang, *J. Fluor. Chem.* **1998**, *87*, 75–83.
[106] M. E. Weeks, *J. Chem. Educ.* **1932**, *9*, 474.
[107] T. Chivers, R. S. Laitinen, *Chem. Soc. Rev.* **2015**, *44*, 1725–1739.
[108] N. Petragnani, H. Stefani, *Tellurium in Organic Synthesis*, Academic Press, Cambridge, MA, **2007**.

[109] F. Wöhler, *Justus Liebigs Ann. Chem.* **1840**, *35*, 111–112.
[110] N. Kambe, K. Kondo, N. Sonoda, *Angew. Chem. Int. Ed.* **1980**, *19*, 1009–1010.
[111] T. Hiiro, N. Kambe, A. Ogawa, N. Miyoshi, S. Murai, N. Sonoda, *Angew. Chem. Int. Ed.* **1987**, *26*, 1187–1188.
[112] N. Kambe, K. Kondo, S. Morita, S. Murai, N. Sonoda, *Angew. Chem. Int. Ed.* **1980**, *19*, 1009.
[113] Y. Aso, T. Nishioka, M. Osuka, K. Nagakawa, K. Sasaki, T. Otsubo, F. Ogura, *J. Chem. Soc. Japan* **1987**, *7*, 1490–1496.
[114] M. Akiba, M. P. Cava, *Synth. Commun.* **1984**, *14*, 1119–1127.
[115] K. Ramasamy, S. Kalyanasundaram, P. Shanmugam, *Synthesis* **1978**, *7*, 545–547.
[116] E. B. R. Prideaux, *J. Chem. Soc. Trans.* **1906**, *89*, 316–332.
[117] J. E. Macintyre, *Dictionary of Inorganic Compounds*, **1992**.
[118] P. M. Watkins, Doctoral Thesis: Studies in the Fluorine Chemistry of Tellurium, University of Leicester, **1968**.
[119] R. Campbell, P. L. Robinson, *J. Chem. Soc.* **1956**, 3454–3458.
[120] W. D. English, J. W. Dale, *J. Chem. Soc.* **1953**, 2498–2499.
[121] H. Bürger, *Z. anorg. allg. Chem.* **1968**, *360*, 97–103.
[122] A. Engelbrecht, W. Loreck, W. Nehoda, *Z. anorg. allg. Chem.* **1968**, *360*, 88–96.
[123] P. M. Watkins, *J. Chem. Educ.* **1974**, *51*, 520.
[124] A. Engelbrecht, F. Sladky, *Adv. Inorg. Chem. Radiochem.* **1981**, *24*, 189–223.
[125] C. Desjardins, C. Lau, J. Passmore, *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 151–153.
[126] G. Klein, D. Naumann, *J. Fluor. Chem.* **1985**, *30*, 259–268.
[127] T. Grelbig, T. Krügerke, K. Seppelt, *Z. anorg. allg. Chem.* **1987**, *544*, 74–80.
[128] K. Alam, A. F. Janzen, *J. Fluor. Chem.* **1985**, *27*, 467–469.
[129] M. Jang, A. F. Janzen, *J. Fluor. Chem.* **1991**, *52*, 45–50.
[130] A. F. Janzen, K. Alam, B. J. Blackburn, *J. Fluor. Chem.* **1989**, *42*, 173–178.
[131] T. M. Klapötke, B. Krumm, K. Polborn, I. Schwab, *J. Am. Chem. Soc.* **2004**, *126*, 14166–14175.
[132] F. V Singh, H. A. Stefani, *Tetrahedron Lett.* **2010**, *51*, 863–867.
[133] L. Engman, J. Persson, *J. Organomet. Chem.* **1990**, *388*, 71–74.
[134] J. Liu, M. Qiu, X. Zhou, *Synth. Commun.* **1990**, *20*, 2759–2767.
[135] X.-J. Zhou, Z.-Z. Huang, *Synth. Commun.* **1989**, *19*, 1347–1349.
[136] T. Sperger, S. Guven, F. Schoenebeck, *Angew. Chem. Int. Ed.* **2018**, *57*, 16903–16906.
[137] E. Pietrasiak, A. Togni, *Organometallics* **2017**, *36*, 3750–3757.
[138] C. Hansch, A. Leo, S. H. Unger, K. H. Kim, D. Nikaitani, E. J. Lien, *J. Med. Chem.* **1973**, *16*, 1207–1216.
[139] M. F. Sowaileh, R. A. Hazlitt, D. A. Colby, *ChemMedChem* **2017**, *12*, 1481–1490.

[140] M. E. Sitzmann, *J. Fluor. Chem.* **1995**, *70*, 31–38.
[141] S. Zhang, L. Kolluru, S. K. Vedula, D. Whippie, J. Jin, *Tetrahedron Lett.* **2017**, *58*, 3594–3597.
[142] G. Perin, L. F. B. Duarte, J. S. S. Neto, M. S. Silva, D. Alves, *Synlett* **2018**, *29*, 1479–1484.
[143] K. Ashley, D. Cordell, D. Mavinic, *Chemosphere* **2011**, *84*, 737–746.
[144] J. Emsley, *The 13th Element : The Sordid Tale of Murder, Fire, and Phosphorus*, Wiley, New York, **2000**.
[145] R. J. VanZee, A. U. Khan, *J. Phys. Chem.* **1976**, *80*, 2240–2242.
[146] A. L. Lavoisier, *Elements of Chemistry*, W. Creech, Edinburgh, **1790**.
[147] J. Wright of Derby, *The Alchemist Discovering Phosphorus*, Derby Museum and Art Gallery, Derby, **1771**.
[148] J. B. Readman, *Process of Obtaining Phosphorus.*, **1888**, US patent 417943.
[149] Z. S. Pentele, V. Hauptgruppe, **n.d.**
[150] S. Jasinski, *Phosphate Rock Statistics and Information*, **2019**.
[151] R. W. Rudolph, R. C. Taylor, R. W. Parry, *J. Am. Chem. Soc.* **1966**, *88*, 3729–3734.
[152] J. G. Morse, J. J. Mielcarek, *J. Fluor. Chem.* **1988**, *40*, 41–49.
[153] N. Arnold, R. Bertermann, F. M. Bickelhaupt, H. Braunschweig, M. Drisch, M. Finze, F. Hupp, J. Poater, J. A. P. Sprenger, *Chem. Eur. J.* **2017**, *23*, 5948–5952.
[154] T. E. Thorpe, *Proc. R. Soc. London* **1877**, *25*, 122–123.
[155] M. S. Whittingham, *Science* **1976**, *192*, 1126–1127.
[156] J. B. Goodenough, M. S. Whittingham, A. Yoshino, *Lithium-Ion Batteries*, Stockholm, **2019**.
[157] A. Yoshino, *Angew. Chem. Int. Ed.* **2012**, *51*, 5798–5800.
[158] M. G. Freire, C. M. S. S. Neves, I. M. Marrucho, J. A. P. Coutinho, A. M. Fernandes, *J. Phys. Chem. A* **2010**, *114*, 3744–3749.
[159] X.-G. Teng, F.-Q. Li, P.-H. Ma, Q.-D. Ren, S.-Y. Li, *Thermochim. Acta* **2005**, *436*, 30–34.
[160] H. Coates, P. R. Carter, *Production of Alkyl Phosphonyl Fluorides*, **1952**, US2853515.
[161] I. P. Komkov, S. Z. Ivin, K. V. Karavano, L. E. Smirno, *Zh. Obs. Khim.* **1962**, *32*, 295–299.
[162] W. C. Smith, *Production of Inorganic Fluorine Compounds*, **1959**, US2904398.
[163] W. C. Smith, *J. Am. Chem. Soc.* **1960**, *82*, 6176–6177.
[164] B. Vabre, K. Chansaenpak, M. Wang, H. Wang, Z. Li, F. P. Gabbaï, *Chem. Commun.* **2017**, *53*, 8657–8659.
[165] E. L. Muetterties, W. Mahler, R. Schmutzler, *Inorg. Chem.* **1963**, *2*, 613–618.
[166] E. L. Muetterties, W. Mahler, K. J. Packer, R. Schmutzler, *Inorg. Chem.* **1964**, *3*, 1298–

1303.
[167] R. Schmutzler, *Inorg. Chem.* **1964**, *3*, 410–415.
[168] G. S. Reddy, R. Schmutzler, *Inorg. Chem.* **1967**, *6*, 823–830.
[169] R. Schmutzler, *Inorg. Chem.* **1964**, *3*, 421–428.
[170] A. J. Arduengo, R. Krafczyk, W. J. Marshall, R. Schmutzler, *J. Am. Chem. Soc.* **1997**, *119*, 3381–3382.
[171] *Nachrichten aus der Chemie* **2014**, *62*, 1111.
[172] J. A. Gibson, R. K. Marat, A. F. Janzen, *Can. J. Chem.* **1975**, *53*, 3044–3052.
[173] W. Sheldrick, *Acta Crystallogr. Sect. B* **1975**, *31*, 1776–1778.
[174] L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Angew. Chem. Int. Ed.* **2012**, *51*, 4714–4717.
[175] L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 2629–2635.
[176] C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374–1377.
[177] L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem. Int. Ed.* **2012**, *51*, 10164–10168.
[178] M. Pérez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 18308–18310.
[179] M. Mehta, I. Garcia de la Arada, M. Perez, D. Porwal, M. Oestreich, D. W. Stephan, *Organometallics* **2016**, *35*, 1030–1035.
[180] A. J. Stepen, M. Bursch, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem. Int. Ed.* **2018**, *57*, 15253–15256.
[181] M. Masaki, K. Fukui, *Chem. Lett.* **1977**, *6*, 151–152.
[182] H. Zhu, Z. W. Qu, S. Grimme, *Chem. Eur. J.* **2019**, *25*, 4670–4672.
[183] R. Bartsch, O. Stelzer, R. Schmutzler, *J. Fluor. Chem.* **1982**, *20*, 85–88.
[184] A. C. Vetter, K. Nikitin, D. G. Gilheany, *Chem. Commun.* **2018**, *54*, 5843–5846.
[185] D. Gwon, D. Lee, J. Kim, S. Park, S. Chang, *Chem. Eur. J.* **2014**, *20*, 12421–12425.
[186] L. P. Hammett, *J. Am. Chem. Soc.* **1937**, *59*, 96–103.
[187] M. J. Frisch, J. A. Pople, J. S. Binkley, *J. Chem. Phys.* **1984**, *80*, 3265–3269.
[188] *All Calculation Were Performed Using the Gaussian 09, Revision D.01 Program Package.*, **n.d.**
[189] C. B. Caputo, D. Winkelhaus, R. Dobrovetsky, L. J. Hounjet, D. W. Stephan, *Dalton Trans.* **2015**, *44*, 12256–12264.
[190] C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, et al., *Org. Lett.* **2005**, *7*, 4277–4280.
[191] G. Doleshall, *J. Organomet. Chem.* **1971**, *30*, 369–375.
[192] Y. Kitamura, M. Matsumura, Y. Murata, M. Yamada, N. Kakusawa, M. Tanaka, H. Okabe, H. Naka, T. Obata, S. Yasuike, *J. Fluor. Chem.* **2017**, *199*, 1–6.

[193] K. V Domasevitch, N. N. Gerasimchuk, A. Mokhir, *Inorg. Chem.* **2000**, *39*, 1227–1237.
[194] G. Schröder, T. Okinaka, Y. Mimura, M. Watanabe, T. Matsuzaki, A. Hasuoka, Y. Yamamoto, S. Matsukawa, K. Akiba, *Chem. Eur. J.* **2007**, *13*, 2517–2529.
[195] M. Cartwright, A. A. Woolf, *J. Fluor. Chem.* **1981**, *19*, 101–122.
[196] M. H. Holthausen, R. R. Hiranandani, D. W. Stephan, *Chem. Sci.* **2015**, *6*, 2016–2021.
[197] M. Mehta, M. H. Holthausen, I. Mallov, M. Pérez, Z.-W. Qu, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2015**, *54*, 8250–8254.
[198] M. H. Holthausen, M. Mehta, D. W. Stephan, *Angew. Chem.* **2014**, *126*, 6656–6659.
[199] M. Pérez, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *Proc. Natl. Acad. Sci.* **2014**, *111*, 10917–10921.
[200] *CrysAlisPro and ABSPACK. Rigaku Oxford Diffraction.*, **2016**.
[201] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122.
[202] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.
[203] G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *71*, 3–8.
[204] O. V Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
[205] J. E. Argüello, L. C. Schmidt, A. B. Peñéñory, *Org. Lett.* **2003**, *5*, 4133–4136.
[206] B. Zeynizadeh, *J. Chem. Res.* **2002**, 564–566.
[207] E. Emer, L. Pfeifer, J. M. Brown, V. Gouverneur, *Angew. Chem. Int. Ed.* **2014**, *53*, 4181–4185.
[208] N. Lu, L. Wang, Z. Li, W. Zhang, *Beilstein J. Org. Chem* **2012**, *8*, 192–200.
[209] Y. Nakai, A. Takahashi, R. Goseki, H. Otsuka, *Polym. Chem.* **2016**, *7*, 4661–4666.
[210] B. Cui, S. Jia, E. Tokunaga, N. Saito, N. Shibata, *Chem. Commun.* **2017**, *53*, 12738–12741.
[211] P. Kirsch, M. Bremer, M. Heckmeier, K. Tarumi, *Angew. Chem. Int. Ed.* **1999**, *38*, 1989–1992.
[212] A. Frischmuth, A. Unsinn, K. Groll, H. Stadtmüller, P. Knochel, *Chem. Eur. J.* **2012**, *18*, 10234–10238.
[213] T. Okazaki, K. K. Laali, S. D. Bunge, S. K. Adas, *Eur. J. Org. Chem.* **2014**, *2014*, 1630–1644.
[214] F. Wang, M. Qu, F. Chen, Q. Xu, M. Shi, *Chem. Commun.* **2012**, *48*, 8580–8582.
[215] T. Morosaki, W.-W. Wang, S. Nagase, T. Fujii, *Chem. Eur. J.* **2015**, *21*, 15405–15411.
[216] J. B. Lambert, S. Zhang, S. M. Ciro, *Organometallics* **1994**, *13*, 2430–2443.
[217] R. R. Holmes, J. M. Holmes, R. O. Day, K. C. Kumara Swamy, V. Chandrasekhar, *Phosphorus. Sulfur. Silicon Relat. Elem.* **1995**, *103*, 153–169.
[218] T. Ono, H. Fukaya, E. Hayashi, H. Saida, T. Abe, P. B. Henderson, R. E. Fernandez,

K. V Scherer, *J. Fluor. Chem.* **1999**, *97*, 173–182.

Appendix

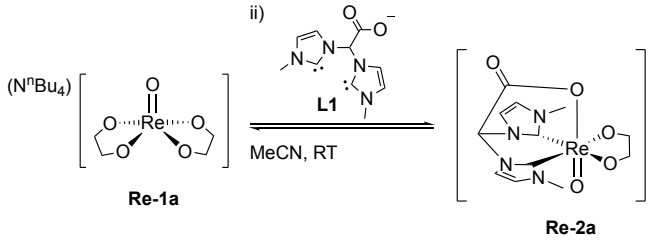
Appendix A: Further Projects

The following section is published as:

Bornemann, D.; Schlemper, L.; Trapp, N.; Togni, A. "Expanding the Scope of Water-Stable Rhenium(V)-NHC Complexes – Synthesis, Characterization, and Derivatization" *Eur. J. Inorg. Chem.* **2020***,* 1004-1010. DOI: 10.1002/ejic.201901077.

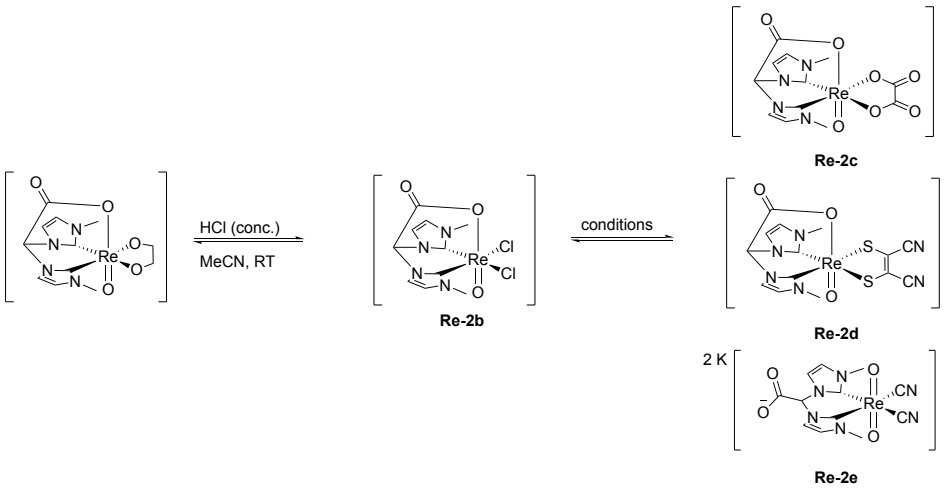
Content:

A synthetic method to access Re(V)-NHC scorpionate complexes was developed. Scorpionate ligand **L1,** containing two NHC donors and one carboxylate moiety, was used in the synthesis of the novel rhenium(V) oxo complex **Re-2a** (Scheme 15).



Scheme 15: Synthesis of **Re-2a** from **Re-1a** and **L1**.

The new complexes were fully characterized by standard spectroscopic means (NMR, UV-vis) as well as mass spectrometry. Furthermore, the solid-state structures were investigated by single crystal XRD analysis. Additionally, their hydrolytic and chemical stability under neutral, basic and acidic aqueous conditions was evaluated. The majority of the complexes shows high water stability. It was shown that complex **Re-2b** can be easily synthesized in a one-pot procedure from $[ReOCl_4]^-$ and is a suitable starting material for the synthesis of [ReO(**L1**)] derivatives (Scheme 16). Thus, the chemistry of the still very small family of Re-NHC complexes was expanded by Re-NHC-scorpionato derivatives.



Scheme 16: Derivatization of **Re-2b** with various ligands. Detailed information of the reaction conditions can be found in the published version.

Appendix B: Abbreviations

aq.	Aqueous
Ar	Aryl
Bu	Butyl
calcd.	Calculated
CCDC	Cambridge Crystallographic Data Centre
DCM	Dichloromethane
DFT	Density functional theory
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
EA	Elemental analysis
e.g.	Example given / for example
equiv./eq.	Equivalents
ESI	eletrospray ionization
Et	Ethyl
EtOAc	Ethyl acetate
EtOH	Ethanol
Et_2O	Diethylether
GC	Gas chromatography
GC-MS	Gas chromatography – mass spectroscopy
h	Hour(s)
HRMS	High resolution mass spectroscopy
Hz	Hertz
^{i}Pr	Isopropyl
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
KF	Potassium Fluoride
Me	Methyl
MeCN	Acetonitrile
MeOH	Methanol
NHC	N-heterocyclic carbene
NMR	Nuclear magnetic resonance
^{n}Bu	*n*-Butyl
ORTEP	Oak Ridge Thermal Ellipsoid Plot
p-TsOH	*para*-Toluenesulfonic acid
Ph	Phenyl
ppm	parts per million

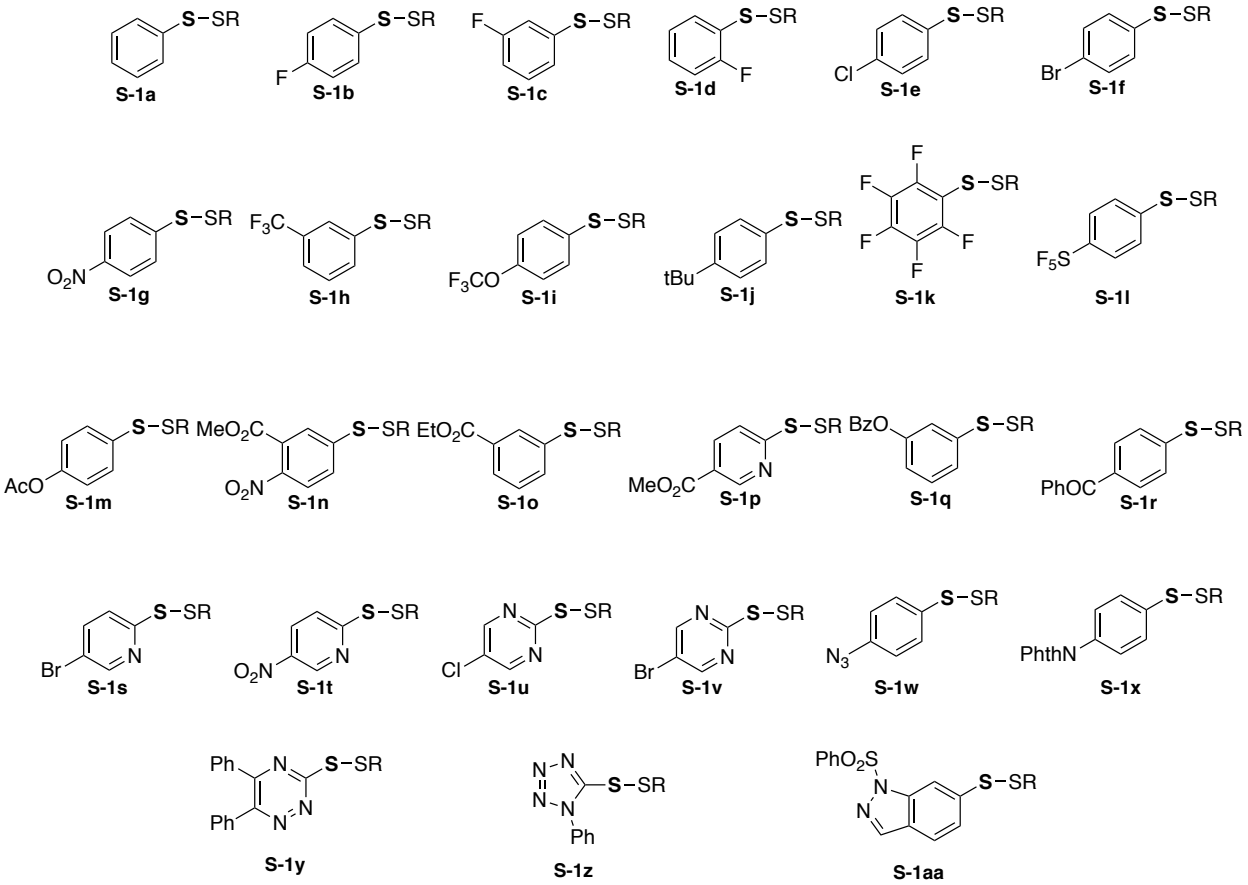
R	Rest
rt	Room temperature
sat.	saturated
SC-XRD	Single crystal X-ray diffraction
t/^{t}	tert
^{t}Bu	Tertiary butyl
TCICA	Trichloroisocyanuric acid
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TMS	Tetramethylsilane
UV	Ultraviolet
XRD	X-ray diffraction

Appendix C: Compound Numbering

Disulfides

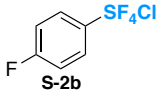
The series of **S-1**-compounds is composed of disulfides. The SR moiety completes each structure to a symmetrical disulfide.

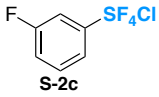
SR = Symmetrical disulfide. Repeated S-arene unit that is drawn out.

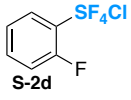


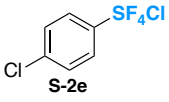
Fluorinated Sulfur Species

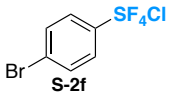

S-2a

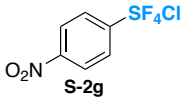

S-2b

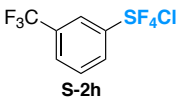

S-2c

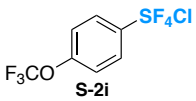

S-2d

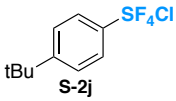

S-2e

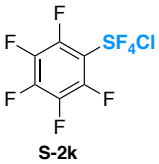

S-2f

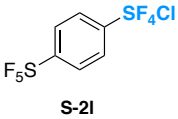

S-2g

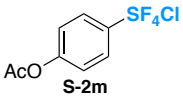

S-2h

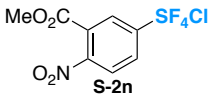

S-2i

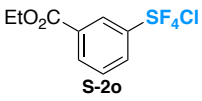

S-2j

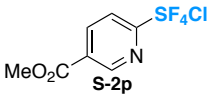

S-2k

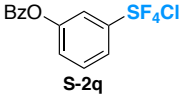

S-2l

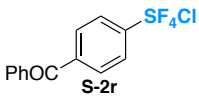

S-2m

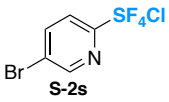

S-2n


S-2o

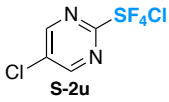

S-2p

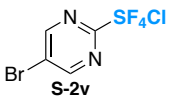

S-2q

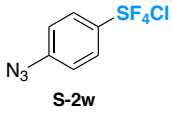

S-2r

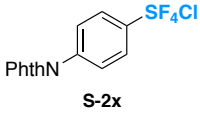

S-2s

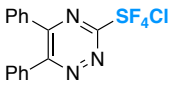

S-2t

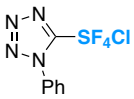

S-2u

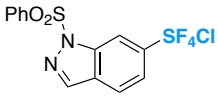

S-2v

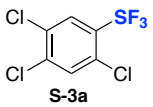

S-2w


S-2x

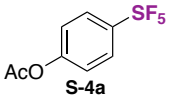

S-2y

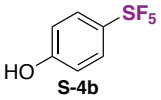

S-2z

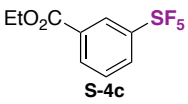

S-2aa


S-3a

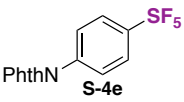

S-3b

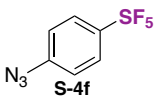

S-4a

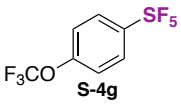

S-4b

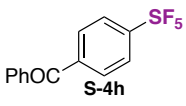

S-4c

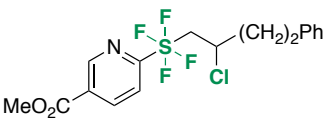

S-4d

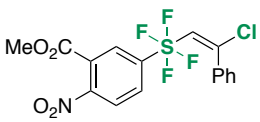

S-4e

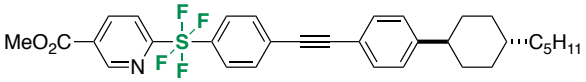

S-4f


S-4g


S-4h


S-5a

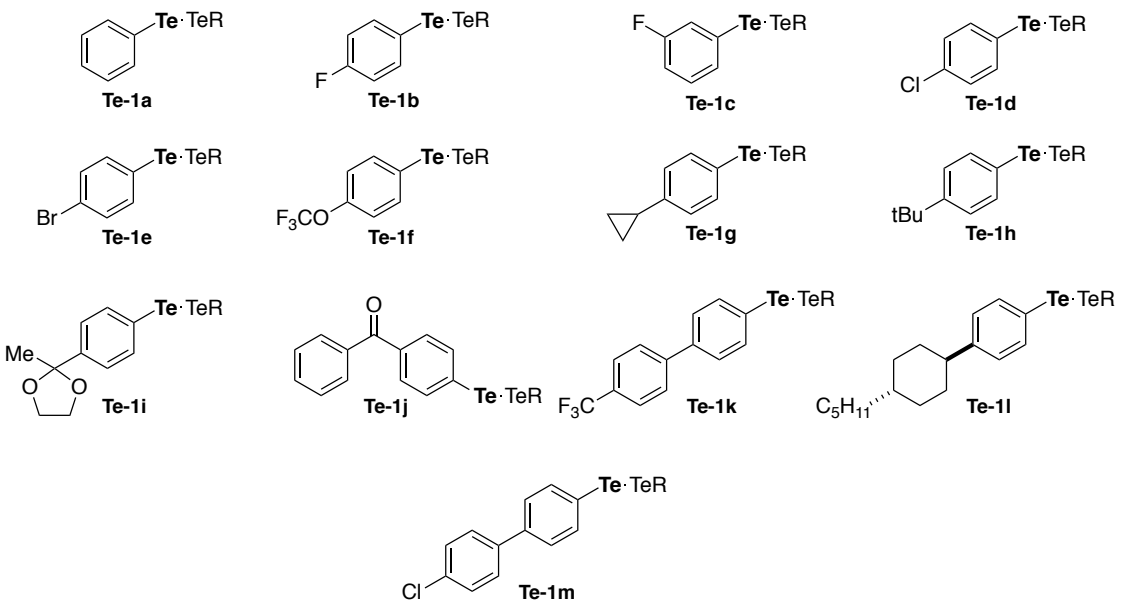

S-5b


S-5c

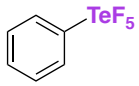
Ditellurides

The series of **Te-1**-compounds is composed of ditellurides. The TeR moiety completes each structure to a symmetrical ditelluride.

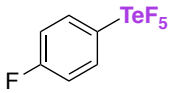
TeR = Symmetrical ditelluride. Repeated Te-arene unit that is drawn out.



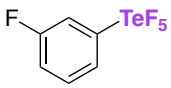
Fluorinated Tellanes and Monotellurides



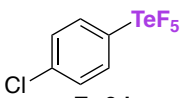
Te-2a



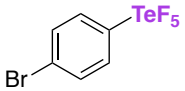
Te-2b



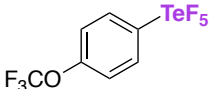
Te-2c



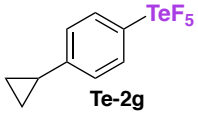
Te-2d



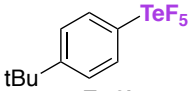
Te-2e



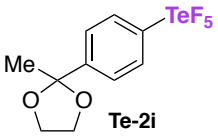
Te-2f



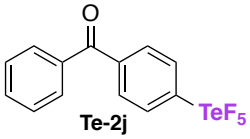
Te-2g



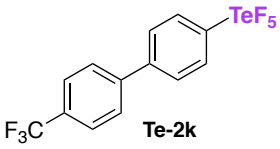
Te-2h



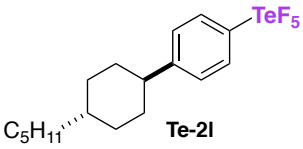
Te-2i



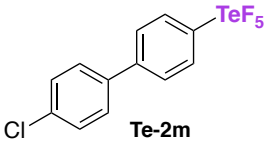
Te-2j



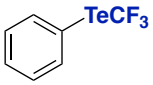
Te-2k



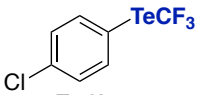
Te-2l



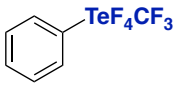
Te-2m



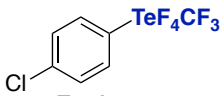
Te-3a



Te-3b

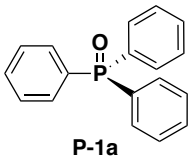


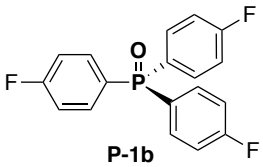
Te-4a

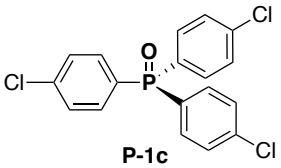


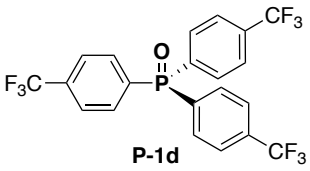
Te-4b

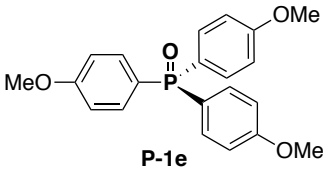
Phosphine oxides

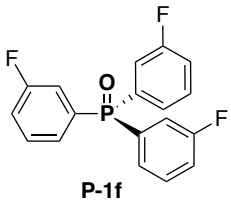

P-1a

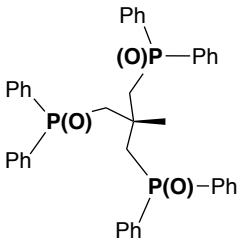

P-1b

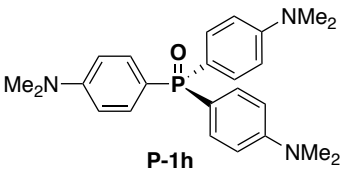

P-1c

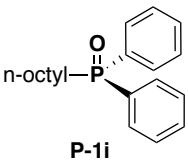

P-1d

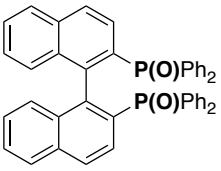

P-1e

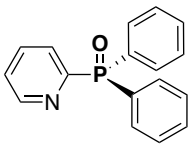

P-1f

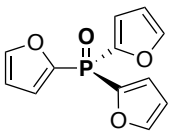

P-1g

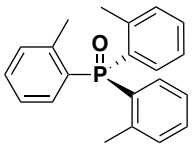

P-1h

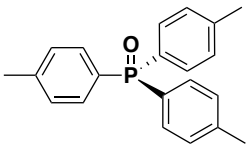

P-1i

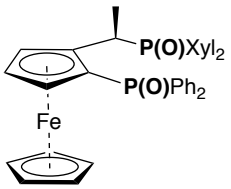

P-1j

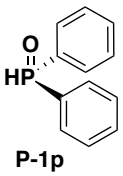

P-1k

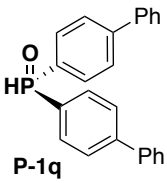

P-1l

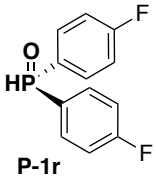

P-1m

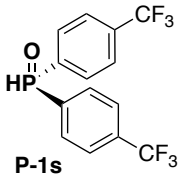

P-1n

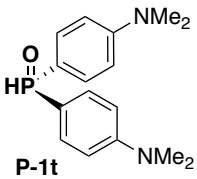

P-1o

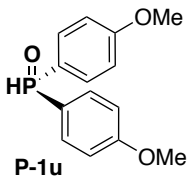

P-1p

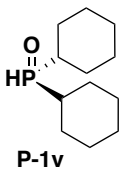

P-1q

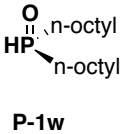

P-1r


P-1s

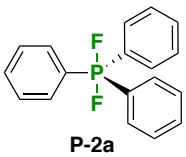

P-1t


P-1u

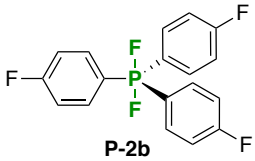

P-1v


P-1w

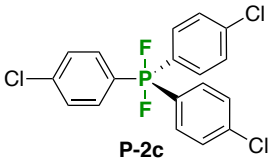
Fluorinated Phosphoranes and Salts thereof



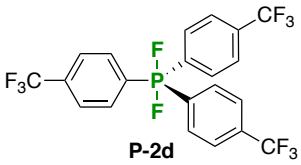
P-2a



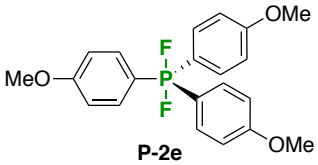
P-2b



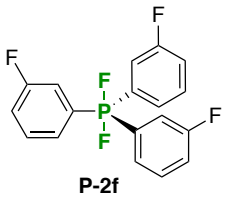
P-2c



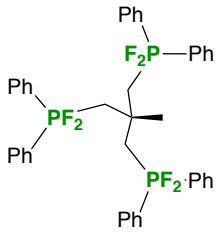
P-2d



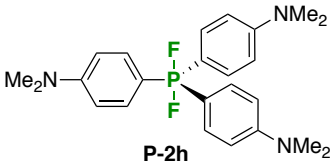
P-2e



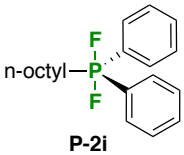
P-2f



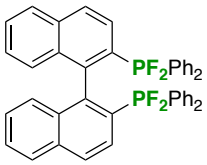
P-2g



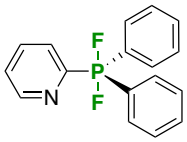
P-2h



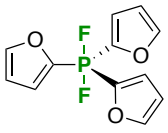
P-2i



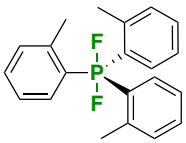
P-2j



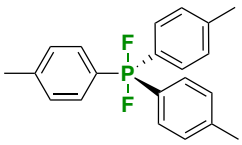
P-2k



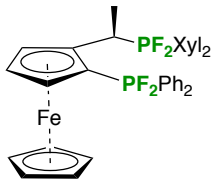
P-2l



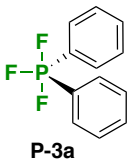
P-2m



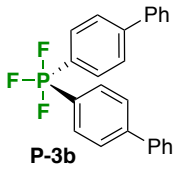
P-2n



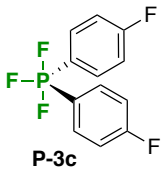
P-2o



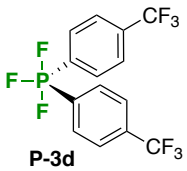
P-3a



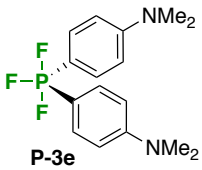
P-3b



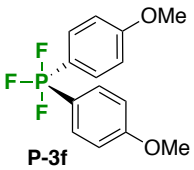
P-3c



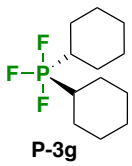
P-3d



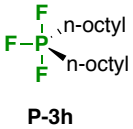
P-3e



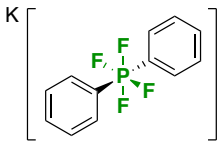
P-3f



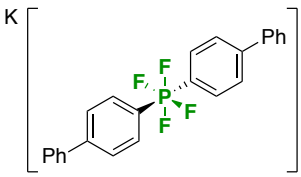
P-3g



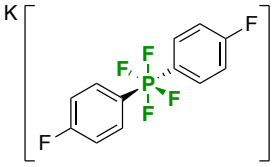
P-3h



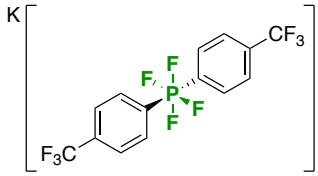
P-4a



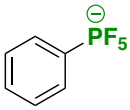
P-4b



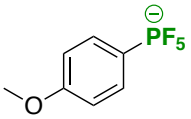
P-4c



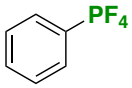
P-4d



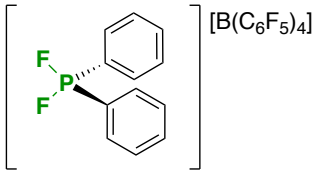
P-5a



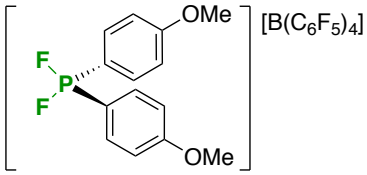
P-5b



P-6a

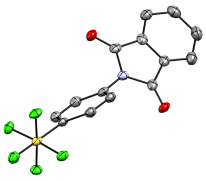
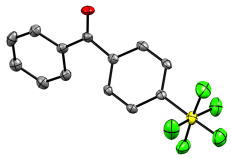
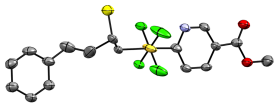


P-7a

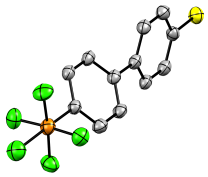


P-7b

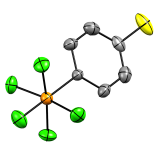
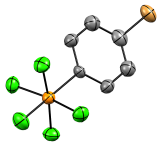
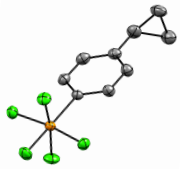
Appendix D: Crystallographic Data

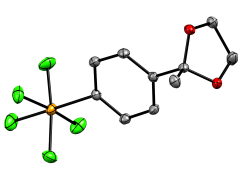
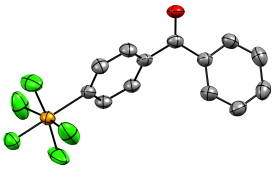
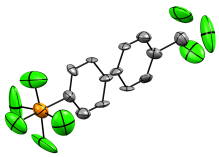




	S-4h	**S-4e**	**S-5b**
CCDC No.	1865800	1865801	1865802
Empirical formula	$C_{14}H_8F_5NO_2S$	$C_{13}H_9F_5OS$	$C_{17}H_{18}ClF_4NO_2S$
Formula weight	349.27	308.26	411.83
Temperature/K	100(2)	100.01	100(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*Cc* (9)	$P2_1/c$ (14)	$P2_1/c$ (14)
a/Å	28.379(9)	7.327(2)	10.555(5)
b/Å	5.7295(19)	6.0995(19)	11.256(5)
c/Å	8.151(3)	27.008(8)	15.009(6)
α/°	90	90	90
β/°	96.636(5)	96.572(5)	103.331(6)
γ/°	90	90	90
Volume/Å^3	1316.4(7)	1199.1(6)	1735.2(13)
Z	4	4	4
ϱ_{calc} g/cm^3	1.762	1.707	1.576
μ/mm^{-1}	0.316	0.326	0.394
F(000)	704	624	848
Crystal size/mm^3	0.36×0.35×0.09	0.45×0.4×0.04	0.47×0.34×0.02
Crystal color	colorless	colorless	colourless
Crystal shape	plate	plate	plate
Radiation	MoK_a (λ=0.71073)	MoK_a (λ=0.71073)	MoK_a (λ=0.71073)
2Θ range/°	5.78 to 51.99	5.60 to 54.00	3.97 to 49.98
Index ranges	-34 ≤ h ≤ 34	-9 ≤ h ≤ 9	-12 ≤ h ≤ 12
	-7 ≤ k ≤ 7	-7 ≤ k ≤ 7	-13 ≤ k ≤ 13
	-10 ≤ l ≤ 10	-31 ≤ l ≤ 34	-17 ≤ l ≤ 17
Reflections collected	6081	15209	22659
Independent reflections	2525	2616	3040
	R_{int} = 0.0369	R_{int} = 0.0606	R_{int} = 0.1489
	R_{sigma} = 0.0440	R_{sigma} = 0.0459	R_{sigma} = 0.0883
Data / Restraints / Param.	2525/2/209	2616/0/181	3040/0/255
Goodness-of-fit on F^2	1.039	1.128	1.088
Final *R* indexes	R_1 = 0.0411	R_1 = 0.0864	R_1 = 0.0596
[$I \geq 2\sigma(I)$]	wR_2 = 0.1020	wR_2 = 0.2074	wR_2 = 0.1363
Final *R* indexes	R_1 = 0.0504	R_1 = 0.1134	R_1 = 0.1609
[all data]	wR_2 = 0.1070	wR_2 = 0.2263	wR_2 = 0.2030



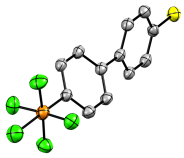
	S-4i
CCDC No.	1922274
Empirical formula	$C_{12}H_8ClF_5S$
Formula weight	314.69
Temperature/K	100.0(1)
Crystal system	triclinic
Space group	*P*-1
a/Å	8.0839(3)
b/Å	8.2186(2)
c/Å	10.1393(5)
α/°	75.023(3)
β/°	68.465(4)
γ/°	88.483(3)
Volume/Å^3	603.57(4)
Z	2
ϱ(calc) g/cm^3	1.732
μ/mm^{-1}	4.899
F(000)	316
Crystal size/mm^3	0.236×0.144×0.068
Crystal color	clear colourless
Crystal shape	block
Radiation	Cu*K*α (λ=1.54184)
2θ range/°	9.73 to 158.95
Index ranges	-10 ≤ h ≤ 10
	-10 ≤ k ≤ 10
	-12 ≤ l ≤ 12
Reflections collected	2715
Independent reflections	2715
	R_{int} = 0.0220
	R_{sigma} = 0.0137
Data/Restraints/Parameters	2715/165/173
Goodness-of-fit on F^2	1.057
Final R indexes [I≥2σ(I)]	R_1 = 0.0789
	wR_2 = 0.2359
Final R indexes [all data]	R_1 = 0.0817
	wR_2 = 0.2413
Largest peak/hole /eÅ^3	0.76/-0.81

			
	Te-2d	**Te-2e**	**Te-2g**
CCDC No.	1922277	1922269	1922276
Empirical formula	$C_6H_4ClF_5Te$	$C_6H_4BrF_5Te$	$C_9H_9F_5Te$
Formula weight	167.07	378.60	339.76
Temperature/K	100.0(2)	100.0(1)	100.0(1)
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	*Cmcm*	*Cmcm*	*P*2/*c*
a/Å	9.8787(5)	9.8395(3)	7.5127(2)
b/Å	12.7936(6)	12.8719(4)	9.9352(2)
c/Å	6.9915(3)	7.1705(2)	13.6517(3)
α/°	90	90	90
β/°	90	90	92.315(2)
γ/°	90	90	90
Volume/Å^3	883.61(7)	908.17(5)	1018.13(4)
Z	4	4	4
ϱ(calc) g/cm^3	2.512	2.769	2.217
μ/mm^{-1}	3.697	31.418	2.957
F(000)	616	688	640
Crystal size/mm^3	0.16×0.16×0.06	0.123×0.057×0.042	0.253×0.165×0.090
Crystal color	clear colourless	clear colourless	clear colourless
Crystal shape	block	block	block
Radiation	Mo*K*α (λ=0.71073)	Cu*K*α (λ=1.54184)	Mo*K*α (λ=0.71073)
2Θ range/°	5.21 to 65.11	11.32 to 157.15	5.07 to 61.00
Index ranges	-14 ≤ h ≤ 14 -17 ≤ k ≤ 19 -10 ≤ l ≤ 10	-12 ≤ h ≤ 11 -15 ≤ k ≤ 16 -8 ≤ l ≤ 7	-10 ≤ h ≤ 10 -14 ≤ k ≤ 14 -19 ≤ l ≤ 19
Reflections collected	5120	2701	42620
Independent reflections	904 R_{int} = 0.0333 R_{sigma} = 0.0262	546 R_{int} = 0.0318 R_{sigma} = 0.0207	3114 R_{int} = 0.0445 R_{sigma} = 0.0158
Data/Restraints/Parameters	904/0/42	546/0/42	3114/1/136
Goodness-of-fit on F^2	1.033	1.128	1.033
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0224 wR_2 = 0.0496	R_1 = 0.0326 wR_2 = 0.0887	R_1 = 0.0176 wR_2 = 0.0416
Final R indexes [all data]	R_1 = 0.0274 wR_2 = 0.0519	R_1 = 0.0332 wR_2 = 0.0891	R_1 = 0.0186 wR_2 = 0.0420
Largest peak/hole /eÅ^3	1922277	1922269	1922276

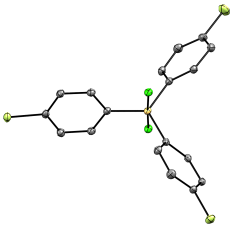
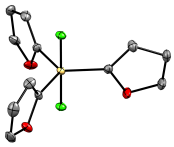
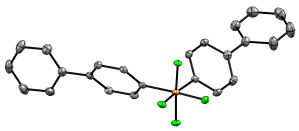




	Te-2i	**Te-2j**	**Te-2k**
CCDC No.	1922270	1922271	1922275
Empirical formula	$C_{10}H_{11}F_5O_2Te$	$C_{13}H_9F_5OTe$	$C_{13}H_8F_8Te$
Formula weight	385.79	403.80	443.79
Temperature/K	100.0(1)	100.0(1)	100.0(1)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$Iba2$
a/Å	6.6004(1)	8.5214(1)	13.8302(1)
b/Å	9.8083(2)	10.3486(1)	14.6762(1)
c/Å	19.4796(2)	15.2187(1)	20.4722(2)
α/°	90	90	90
β/°	98.928(1)	98.041(1)	90
γ/°	90	90	90
Volume/Å^3	1245.80(2)	1328.86(2)	4155.34(6)
Z	4	4	12
ϱ(calc) g/cm^3	2.057	2.018	2.128
μ/mm^{-1}	19.427	18.202	17.806
F(000)	736	768	2520
Crystal size/mm^3	0.159×0.141×0.092	0.188×0.181×0.133	0.167×0.130×0.080
Crystal color	clear colourless	clear colourless	clear colourless
Crystal shape	block	block	block
Radiation	CuKα (λ=1.54184)	CuKα (λ=1.54184)	CuKα (λ=1.54184)
2θ range/°	9.19 to 159.17	10.37 to 159.27	8.64 to 159.41
Index ranges	-8 ≤ h ≤ 8	-10 ≤ h ≤ 10	-17 ≤ h ≤ 17
	-12 ≤ k ≤ 12	-12 ≤ k ≤ 13	-18 ≤ k ≤ 18
	-24 ≤ l ≤ 24	-19 ≤ l ≤ 19	-26 ≤ l ≤ 25
Reflections collected	37615	35967	55264
Independent reflections	2694	2865	4485
	R_{int} = 0.0454	R_{int} = 0.0507	R_{int} = 0.0559
	R_{sigma} = 0.0156	R_{sigma} = 0.0168	R_{sigma} = 0.0236
Data/Restraints/Parameters	2694/17/174	2865/0/181	4485/1480/584
Goodness-of-fit on F^2	1.100	1.110	1.053
Final R indexes [I≥2σ(I)]	R_1 = 0.0203	R_1 = 0.0219	R_1 = 0.0349
	wR_2 = 0.0514	wR_2 = 0.0560	wR_2 = 0.0828
Final R indexes [all data]	R_1 = 0.0205	R_1 = 0.0223	R_1 = 0.0369
	wR_2 = 0.0515	wR_2 = 0.0563	wR_2 = 0.0844
Largest peak/hole /eÅ^3	0.36/-0.83	0.33/-0.64	0.30/-0.64

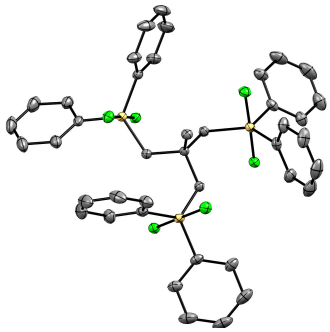




	Te-4b	**Te-4b**	**Te-2m**
CCDC No.	1922278	1922273	1922272
Empirical formula	$C_7H_4ClF_7Te$	$C_7H_4ClF_7Te$	$C_{12}H_8ClF_5Te$
Formula weight	384.15	384.15	410.23
Temperature/K	100.0(1)	100.0(1)	100.0(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a/Å	6.9132(2)	6.9100(1)	8.1936(18)
b/Å	8.3079(2)	8.3075(2)	8.1938(18)
c/Å	10.3896(2)	10.3845(2)	10.549(2)
α/°	105.937(2)	105.930(2)	111.030(3)
β/°	98.882(2)	98.848(2)	101.621(3)
γ/°	107.713(2)	107.692(2)	93.473(3)
Volume/Å^3	527.82(2)	527.49(2)	640.6(2)
Z	2	2	2
ϱ(calc) g/cm^3	2.417	2.419	2.127
μ/mm^{-1}	25.334	3.140	2.572
F(000)	356	356	388
Crystal size/mm^3	0.168×0.094×0.04	0.197×0.128×0.055	0.15×0.13×0.12
Crystal color	clear colourless	clear colourless	clear colourless
Crystal shape	plate	plate	prism
Radiation	Cu*K*α (λ=1.54184)	Mo*K*α (λ=0.71073)	Mo*K*α (λ=0.71073)
2Θ range/°	9.17 to 159.90	5.48 to 69.56	4.26 to 56.69
Index ranges	-8 ≤ h ≤ 8	-11 ≤ h ≤ 10	-10 ≤ h ≤ 10
	-10 ≤ k ≤ 10	-13 ≤ k ≤ 13	-10 ≤ k ≤ 10
	-13 ≤ l ≤ 13	-16 ≤ l ≤ 16	-13 ≤ l ≤ 14
Reflections collected	15959	31695	5605
Independent reflections	2212	4243	3109
	R_{int} = 0.0598	R_{int} = 0.0512	R_{int} = 0.0246
	R_{sigma} = 0.0302	R_{sigma} = 0.0265	R_{sigma} = 0.0420
Data/Restraints/Parameters	2212/0/145	4243/0/145	3109/0/172
Goodness-of-fit on F^2	1.163	1.090	1.089
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0303	R_1 = 0.0289	R_1 = 0.0344
	wR_2 = 0.0861	wR_2 = 0.0724	wR_2 = 0.0766
Final R indexes [all data]	R_1 = 0.0311	R_1 = 0.0311	R_1 = 0.0389
	wR_2 = 0.0866	wR_2 = 0.0731	wR_2 = 0.0788
Largest peak/hole /eÅ^3	1.64/-1.50	1.45/-1.67	1.28/-0.89

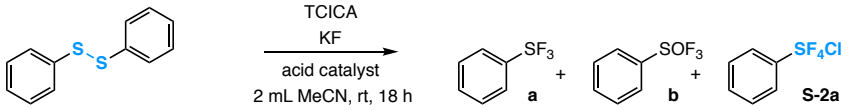
	P-2c	**P-2l**	***cis*-P-4b**
CCDC No.	2013558	2013559	2013560
Empirical formula	$C_{18}H_{12}Cl_3F_2P$	$C_{12}H_9F_2O_3P$	$C_{100}H_{78}F_{16}K_4N_2P_4$
Formula weight	403.60	270.16	1891.92
Temperature/K	100.0(1)	100.0(1)	100.0(1)
Crystal system	triclinic	monoclinic	triclinic
Space group	*P*-1 (2)	*C*2/*c* (15)	*P*-1 (2)
a/Å	9.7365(5)	13.9997(19)	11.8241(7)
b/Å	10.2858(6)	8.1018(13)	17.4794(11)
c/Å	18.6100(4)	10.9857(15)	21.2819(13)
α/°	82.830(3)	90	90.796(2)
β/°	86.990(3)	114.377(4)	96.387(1)
γ/°	68.701(5)	90	90.001(2)
Volume/Å^3	1722.8(2)	1134.9(3)	4370.8(5)
Z	4	4	2
ρ_{calc} g/cm^3	1.556	1.581	1.438
μ/mm^{-1}	5.856	0.266	0.362
F(000)	816	552	1944
Crystal size/mm^3	0.21×0.19×0.09	0.2×0.05×0.05	0.17×0.12×0.09
Crystal color	clear colourless	clear colourless	clear colourless
Crystal shape	block	needle	block
Radiation	Cu K_a (λ=1.54184)	MoK_a (λ=0.71073)	MoK_a (λ=0.71073)
2Θ range/°	4.79 to 159.70	5.96 to 54.97	3.00 to 61.18
Index ranges	-12 ≤ h ≤ 12	-15 ≤ h ≤ 18	-16 ≤ h ≤ 16
	-11 ≤ k ≤ 12	-10 ≤ k ≤ 10	-25 ≤ k ≤ 25
	-23 ≤ l ≤ 23	-13 ≤ l ≤ 14	-30 ≤ l ≤ 30
Reflections collected	47132	5613	102687
Independent reflections	7309	1313	26732
	R_{int} = 0.0376	R_{int} = 0.0311	R_{int} = 0.0579
	R_{sigma} = 0.0211	R_{sigma} = 0.0252	R_{sigma} = 0.0598
Data / Restraints / Param.	7309/0/433	1313/85/129	26732/0/1137
Goodness-of-fit on F^2	1.056	1.030	0.999
Final *R* indexes	R_1 = 0.0289	R_1 = 0.0327	R_1 = 0.0422
[$I \geq 2\sigma(I)$]	wR_2 = 0.0747	wR_2 = 0.0794	wR_2 = 0.0836
Final *R* indexes	R_1 = 0.0302	R_1 = 0.0436	R_1 = 0.0763
[all data]	wR_2 = 0.0756	wR_2 = 0.0849	wR_2 = 0.0951
Largest peak/hole /eÅ^3	0.37/-0.36	0.46/-0.24	0.76/-0.36



	P-2g
CCDC Code	2015080
Empirical formula	$C_{41}H_{39}F_6P_3$
Formula weight	738.63
Temperature/K	100.0(1)
Crystal system	cubic
Space group	*Pa*-3 (205)
a/Å	19.4010(3)
b/Å	19.4010(3)
c/Å	19.4010(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	7302.52(4)
Z	8
ϱ_{calc} g/cm^3	1.344
μ/mm^{-1}	2.009
F(000)	3072
Crystal size/mm^3	0.266×0.215×0.117
Crystal color	clear colourless
Crystal shape	block
Radiation	Cu K_a (λ=1.54184)
2Θ range/°	7.89 to 159.88
Index ranges	-24 ≤ h ≤ 24
	-24 ≤ k ≤ 24
	-24 ≤ l ≤ 24
Reflections collected	205577
Independent reflections	2673
	R_{int} = 0.0503
	R_{sigma} = 0.0080
Data / Restraints / Param.	2673/0/152
Goodness-of-fit on F^2	1.069
Final *R* indexes	R_1 = 0.0353
[$I \geq 2\sigma(I)$]	wR_2 = 0.0883
Final *R* indexes	R_1 = 0.0356
[all data]	wR_2 = 0.0885
Largest peak/hole /eÅ^3	0.42/-0.32

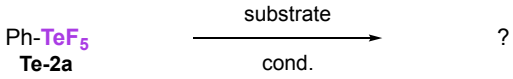
Appendix E: Additional Tables

Table 24: Detailed screening data for the synthesis of **S-2a** using TCICA/KF.



entry	*TCICA (equiv.)*	*KF (equiv.)*	*TFA (equiv.)*	*additive (equiv.)*	***a** yield (%)*	***b** yield (%)*	***S-2a** yield (%)*	**a** : **b** : **c**	*notes*
1	9	16	-	-	9	0	0	-	-
2	9	16	0.5	-	18	24	36	1 : 1.3 : 2.0	72 h
3	18	32	0.5	-	10	29	47	1 : 2.9 : 4.7	-
4	27	48	0.5	-	3	5	trace	1 : 1.6 : trace	4 mL MeCN
5	9	16	0.5	-	26	29	30	1 : 1.1 : 1.2	-
6	18	9	0.5	-	9	28	28	1 : 3.1 : 3.1	-
7	27	9	0.5	-	1	8	trace	1 : 8.0 : trace	4 mL MeCN
8	9	16	0.5	-	25	27	32	1 : 1.1 : 1.3	-
9	9	16	1.0	-	21	42	19	1 : 2.0 : 0.9	-
10	9	16	2.0	-	6	47	3	1 : 7.8 : 0.5	-
11	9	16	0.5	-	16	31	trace	1 : 1.9 : trace	KF not dried
12	9	16	0.5	-	22	33	27	1 : 1.5 : 1.2	-
13	9	16	0.5	-	29	11	14	1 : 0.4 : 0.5	1 mL MeCN
14	9	16	0.5	-	0	0	0	-	$MeNO_2$ solvent
15	9	16	0.5	-	30	9	21	1 : 0.3 : 0.7	EtOAc solvent
16	9	16	0.1	-	24	10	48	1 : 0.4 : 2.0	-
17	9	16	-	$FeCl_3$ (0.5)	0	0	0	-	-
18	9	16	-	$ZnCl_2$ (0.5)	27	19	37	1 : 0.7 : 1.4	-
19	9	16	-	CuCl (0.5)	30	3	21	1 : 0.1 : 0.7	-
20	4.5	8.0	0.25	-	21	7	2	1 : 0.3 : 0.1	thiophenol subs.
21	9	16	0.1	-	25	9	45	1 : 0.4 : 1.8	-
22	**18**	**32**	**0.1**	**-**	**9**	**13**	**70**	**1 : 1.4 : 7.8**	**-**
23	9	16	0.05	-	25	7	46	1 : 0.3 : 1.8	-
24	9	16	-	$ZnCl_2$ (0.1)	28	11	48	1 : 2.5 : 1.7	-
25	18	32	-	$ZnCl_2$ (0.1)	13	16	65	1 : 1.2 : 5.0	-
26	9	16	-	$ZnCl_2$ (0.05)	28	6	42	1 : 0.2 : 1.5	-
27	9	16	0.1 (anhydride)*	-	30	8	41	1 : 0.3 : 1.4	*used TFAA
28	18	16	0.1	-	7	7	40	1 : 1.0 : 5.7	-
29	18	24	0.1	-	7	6	50	1 : 0.9 : 7.1	-
30	18	32	0.1	-	9	7	69	1 : 0.8 : 7.7	-
31	18	16	0.1	$CaCl_2$ (1.0)	13	10	18	1 : 0.8 : 3.0	-
32	18	24	0.1	$CaCl_2$ (1.0)	7	13	41	1 : 1.9 : 5.9	-
33	18	32	0.1	$CaCl_2$ (1.0)	6	12	57	1 : 2.0 : 9.5	-
34	18	16	0.1	$CaCl_2$ (4.0)	6	23	25	1 : 3.8 : 4.2	-
35	18	24	0.1	$CaCl_2$ (4.0)	6	25	30	1 : 4.2 : 5.0	-
36	18	32	0.1	$CaCl_2$ (4.0)	6	30	33	1 : 5.0 : 5.5	-
37	18	32	0.1	-	9	10	61	1 : 1.1 : 6.8	-
38	18	40	0.1	-	7	10	66	1 : 1.4 : 9.4	-
39	18	48	0.1	-	8	11	69	1 : 1.4 : 8.6	-
40	18	32	0.1	-	7	10	57	1 : 1.4 : 8.1	-
41	18	32	0.1	TBACl (0.1)	13	8	48	1 : 0.6 : 3.7	-
42	18	32	0.1	TBACl (1.0)	13	4	51	1 : 0.3 : 3.9	-
43	18	32	0.1	TBACl (5.0)	18	trace	44	1 : trace: 2.4	-
44	18*	32	0.1	-	0	0	0	-	*used NCS
45	18*	32	0.1	-	0	0	0	-	*used N-chloro-phthalimide

Table 25: Screening data of the reactions between **Te-2a** and various substrates.



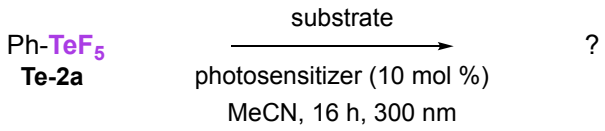
entry	*reactant*	*solvent*	*conditions*	*conversion (%)*
1	pyridinium tetrafluoroborate	MeCN	rt, 3 h	0
2	*tert*-butanol	MeCN	rt, 48 h	0
3	hexafluoroisopropanol	DCM	rt, 15 h	0
4	lithium dimethylamide	DCM	rt, 15 h	0
5	lithium dimethylamide	MeCN	rt, 15 h	74[a]
6	sodium methoxide	DCM	rt, 15 h	76[b]
7	acenaphtylene	DCM	60°C, 20 h	0
8	phenylacetylene	DCM	60°C, 20 h	0
9	hept-1-yne	DCM	60°C, 20 h	0
10	cyclohexene	DCM	60°C, 20 h	0
11	octa-1,7-diene	DCM	60°C, 20 h	0
12	trifluoromethyl(trimethylsilane)	MeCN	rt, 15 h	0[c]
13	silver(I) trifluoromethanethiolate	MeCN	rt, 15 h	0
14	potassium cyanide	DCM	rt, 15 h	0
15	potassium cyanide	MeCN	rt, 15 h	0
16	*tert*-butyl isocyanide	DCM	rt, 15 h	0
17	*tert*-butyl isocyanide	MeCN	rt, 15 h	0
18	potassium thiocyanate	DCM	rt, 15 h	0
19	potassium thiocyanate	MeCN	rt, 15 h	0
20	sodium hydride	DCM	rt, 15 h	0
21	sodium hydride	MeCN	rt, 15 h	0
22	phenyllithium	THF	rt, 15 h	0
23	methyllithium	THF	rt, 15 h	0
24	trifluoromethyl(trimethylsilane)	MeCN	rt to reflux, 48 h	0
25	trifluoromethyl(trimethylsilane)	DCM	rt to reflux, 48 h	0
26	difluoromethyl(trimethylsilane)	MeCN	rt to reflux, 48 h	0
27	difluoromethyl(trimethylsilane)	DCM	rt to reflux, 48 h	0
28	pentafluoroethyl(trimethylsilane)	MeCN	rt to reflux, 48 h	0
29	pentafluoroethyl(trimethylsilane)	DCM	rt to reflux, 48 h	0
30	trimethylsilylacetylene	MeCN	rt to reflux, 48 h	0
31	trimethylsilylacetylene	DCM	rt to reflux, 48 h	0
32	trimethylsilyl cyanide	MeCN	rt to reflux, 48 h	0
33	trimethylsilyl cyanide	DCM	rt to reflux, 48 h	0

[a]Product from substitution of a single equatorial fluorine atom on **Te-2a** with -NMe_2 (i.e. formation of the *cis*-isomer). ^{19}F NMR data in CD_3CN: -34.03 (1F, dt, *J* = 150.6 Hz, 105.0 Hz), -47.35 (1F, dddsept, *J* = 150.6 Hz, 124.0 Hz, 120.8 Hz, 4.9 Hz), -74.32 (2F, dd, *J* = 122.8 Hz, 105.0 Hz). An unidentified byproduct accounts for the rest of the mass balance.

[b]Product from substitution of a single equatorial fluorine atom on **Te-2a** with -OMe (i.e. formation of the *cis*-isomer). ^{19}F NMR data in CD_3CN: -45.20 (1F, ddd, *J* = 148.8 Hz, 108.3 Hz, 104.1 Hz) -50.14 (1F, ddd, *J* = 148.8 Hz, 136.9 Hz, 127.0 Hz Hz) -59.45 (2F, ddd, *J* = 139.9 Hz, 108.3 Hz, 6.8 Hz). Unreacted **Te-2a** accounts for the rest of the mass balance.

[c]Reaction performed with and without 1.0 eq. CsF.

Table 26: Screening data of the reactions between **Te-2a** and various substrates under photoredox conditions.



entry	*reactant*	*sensitizer*	*conversion (%)*
1a)	indene	-	0
1b)	indene	benzophenone	0
1c)	indene	9-fluorenone	0
2a)	styrene	-	0
2b)	styrene	benzophenone	0
2c)	styrene	9-fluorenone	0
3a)	phenylacetylene	-	0
3b)	phenylacetylene	benzophenone	0
3c)	phenylacetylene	9-fluorenone	0
4	benzil	-	0
5a)	2-cyclohexen-1-one	-	0
5b)	2-cyclohexen-1-one	benzophenone	0
6a)	1-methylimidazole	-	0
6b)	1-methylimidazole	benzophenone	0
7	sodium azide	-	54% (*cis*:*trans* 1.6:1.0)[a]
8	adamantane	-	0

[a]Products from substitution of a single fluorine atom on **Te-2a** with $-N_3$ (i.e. formation of both the *cis*- and *trans*-isomers). ^{19}F NMR data in CD_3CN: (*trans*) -45.68 (4F, s); (*cis*) -30.56 (1F, ddd, J = 145.2 Hz, 136.9 Hz, 132.7 Hz) -48.88 (1F, m), -53.02 (2F, ddd, J = 136.9 Hz, 89.3 Hz, 7.1 Hz). A minor unidentified byproduct was also observed in the crude reaction mixture.

Curriculum Vitae

Dustin Bornemann
Blümlisalpstrasse 33, 8006 Zürich (CH)
dustin_bornemann@hotmail.de, +41 76 496 56 79
22.11.1991 in Stendal (GER)

Education

July 2017 – November 2020	**Doctoral Studies in Chemistry** Advisor: Prof. Antonio Togni	ETH Zurich
September 2015 – November 2016	**M.Sc. in Chemistry** Advisor: Prof. Roger Alberto	University of Zurich
September 2012 – July 2015	**B.Sc. in Chemistry**	University of Zurich
2008 – 2011	**Eidgenössische Matura**	Kantonsschule Baden

Extracurricular Research Experience

November 2016 – April 2017	**Postgraduate Researcher**	Novartis AG, Basel

Supervision Activities

July 2017 – May 2019	Supervision of an Apprenticeship for Laboratory Technicians Apprentice: Sebastian Küng
January– May 2018	Supervision of a Master Level Semester Project "Water-Stable Re(V)-NHC Complexes". Student: Lukas Schlemper
January– May 2019	Supervision of a Master Level Semester Project "Synthesis of $ArTeF_5$ Compounds". Student: Carmen Ziegler
January– August 2019	Supervision of a Master Thesis "Re(V)-NHC Scorpionate Complexes". Student: Lukas Schlemper
September – December 2019	Supervision of a Master Level Semester Project "Synthesis of Fluorophosphoranes". Student: Lionel Wettstein
July – December 2020	Supervision of a Master Thesis "Highly Fluorinated Tellanes and their Salts". Student: Lionel Wettstein

Teaching Activities

September – December 2015	Organic Chemistry Lab Course (TA)
February – June 2016	Inorganic Chemistry Lab Course (TA)
September – December 2017	Inorganic Chemistry Lab Course (TA)
September – December 2017	Intro Inorganic Chemistry I (Head TA)
September – December 2018	Intro Inorganic Chemistry I (Head TA)
September – December 2019	Intro Inorganic Chemistry I (Head TA)
September – December 2020	Intro Inorganic Chemistry I (Head TA)