氏　　名	ダス　プロジェリタ DAS PRAJWALITA
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学位論文題目	Design of Methodologies for the Synthesis of Novel Organo-Fluoro-Sulfur Compounds （新規含フッ素－硫黄化合物の設計および合成法の開発）
論文審査委員	主査　教授　山下　啓司 教授　柴田　哲男 教授　林　秀敏 （名古屋市立大学）

論文内容の要旨

The field of organo-fluoro-sulfur chemistry have undergone tremendous progress in the past several decades. However, new and advanced methodologies, and new interesting molecules are always sought after, which can overcome the drawbacks of the reported literature and provide suitable compounds for drug and material exploration. This thesis describes our contribution to the field of organo-fluoro-sulfur chemistry with the development of new methodologies for late stage fluorination. We have synthesized new reagents for the insertion of pyridine-SF_5, Aryl-SO_2CF_3, pyridine-SO_2CF_3 groups into organic moieties. Also, we have analysed the bioactive behaviour of several fluorinated compounds against tumor cells. And finally, we have synthesized a variety of pyridine-SF_4-derivatives, a group which is highly underdeveloped and has been lying dormant for years.

Chapter 1 reveals the synthesis of pentafluorosulfanyl (SF_5)-pyridylaryl-λ^3-iodonium salts, which acts as electrophilic reagents for the insertion of the pyridine-SF_5-moiety by transfer pyridylation. These reagents are shelf stable and mild, which rids chemists from using the harsh reaction conditions and special equipment for the synthesis of pyridine-SF_5 compounds. Use of these reagents under mild conditions can lead to insertion of pyridine-SF_5 moiety into *C*-, *N*-, *O*- and *S*-nucleophiles.

Chapter 2 tackles with the issue of regioselective substitution on the aryl/pyridyl-SO_2CF_3 compounds by the use of triflyl-aryl/pyridyl□λ^3□iodonium salts as electrophilic reagents. Use of these shelf stable and mild reagents lead to the chemoselective transfer of the aryl/pyridyl-SO_2CF_3 group to attacking nucleophiles, namely *C*-, *N*-, *O*- and *S*-nucleophiles, providing products in good to excellent yields.

Chapter 3 is an investigation of the bioactive efficiency of various fluorinating reagents, especially focussing on fluorinated-hypervalent iodine reagents. The bioactivity of the compounds was analysed against human leukemic monocyte lymphoma U937 cells and good efficiency was observed for *ortho*-fluorinated diaryliodonium salts, especially, the newly synthesized *ortho*-SF_5-diaryl-λ^3-iodonium salt.

Chapter 4 describes the synthesis of Pyridne-SF_4-adducts for the first time *via* radical reactions. The most interesting feature of this work was the stability of the pyridine-SF_4-addition products, unlike the benzene analogues. DFT investigation revealed that the pyridine-analogues were thermodynamically stable than the benzene ones. Thus, the stable pyridine-SF_4-alkynes were used for 1,3-cycloadditions to provide interesting SF_4-bridged pyridine and triazole compounds, which can be attractive molecules for medicinal investigation.

Chapter 5 summarizes the complete work, which is been described in the thesis.

Chapter 6 is the experimental section, which provides detailed experimental procedures and characterization of the new compounds.

論文審査結果の要旨

The past several decades have seen tremendous progress in the field of organo-fluoro-sulfur chemistry. However, new and advanced techniques, and new interesting molecules are always sought after, which can overcome the drawbacks of the reported procedures and provide suitable compounds for drug and material exploration. This thesis describes our contribution to the field of organo-fluoro-sulfur chemistry with the development of new methodologies for late stage fluorination. We have synthesized new reagents for insertion of pyridine-SF_5, Aryl-SO_2CF_3, pyridine-SO_2CF_3 groups into organic moieties. Also, we have analysed the bioactive behaviour of several fluorinated compounds. And finally, we have synthesized a variety of pyridine-SF_4-derivatives, a group which had been lying dormant for many years.

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以上のように，本論文では新規含フッ素-硫黄化合物の設計および合成法の開発に成功した。これらは，4編の有審査論文（うち，第1著者4編）としてまとめられている。よって，本論文は，学位論文として十分価値あるものと認められる。