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学位論文題目	Development of Novel Synthetic Methodologies for Pentafluorosulfanyl Compounds （ペンタフルオロスルファニル化合物の新合成手法の開発）
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 initial report of SF_5-arenes appeared in the 1960s, but SF_5-group chemistry remained a "sleeping beauty" for the first 40 years. The SF_5 group, reasonably referred to as the "super-trifluoromethyl group", with intrinsically superior physicochemical properties, is currently being deployed to alter the physicochemical properties of drug-like molecules, while the application of SF_5-containing compounds is largely limited due to the lack of synthetic accessibility. This thesis describes our investigation in the preparation of SF_5 group containing compounds. We have developed the first general method for the synthesis of *m*-and *p*-SF_5-pyridines and functionalization of SF_5-pyridines by nucleophilic aromatic substitution reactions. Later, we disclosed the Cl-F exchange reaction of electron-deficient (hetero)arene-SF_4Cl could be successfully initiated in high yields through the use of IF_5 inhibiting a major side reaction of C-S bond cleavage. Finally, a novel approach for the silver-mediated self-immolative Cl-F

exchange fluorination of arylsulfur chlorotetrafluorides Ar-SF_4Cl to arylsulfur pentafluorides Ar-SF_5 was achieved by a unique self-immolative fashion.

In chapter 1, briefly introducing "future star" group, SF_5 group, the properties, the applications in pharmaceuticals and materials and the methods for the synthesis of SF_5-containing compounds.

In chapter 2, a practical method to access *m*-and *p*-SF_5-substituted pyridines has been developed by two-step procedure involving SF_4Cl-pyridine synthesis by the oxidative chlorotetrafluorination of pyridine disulfides with a Cl_2/KF/CH_3CN system, followed by AgF mediated chloride-fluoride exchange reaction. The effect of fluorine on the successful oxidative chlorotetrafluorination of *meta*- and *para*-substituted pyridine disulfides have been studied. The 2-fluorinated SF_5-pyridines could react with nucleophiles under suitable conditions through S_NAr substitution to provide 2-substituted pyridine derivatives.

In chapter 3, The Cl-F exchange reaction of (hetero)aryl sulfur chlorotetrafluorides is notorious difficulty in the synthesis of SF_5-arenes. We found a simple and powerful method under the IF_5 as fluorine reagent in the Cl-F exchange reaction for the synthesis of electron deficient SF_5-arenes and heteroarenes in good to high yields. The key to success is a halogen bond between F and I with the process in the Cl-F exchange reaction of arene-SF_4Cl via S_Ni-like substitution. The synthesis of *o*-SF_5-pyridines having NO_2 or CF_3 substituents, and SF_5-pyrimides, was achieved for the first time by the IF_5 method.

In chapter 4, the first fluorinating reagent-free-transformation of Ar-SF_4Cl into Ar-SF_5 was disclosed in the presence of silver carbonate. The substrate and functional group generality of this method are wide, and even heteroaryl SF_4Cl such as pyridine is tolerated, with moderate to good yields. The feature of this unique transformation is the self-immolation of $ArSF_4Cl$. This method can be applied in the Suzuki-coupling and Miyaura borylation under a one-pot conversion in an environmentally benign solvent Solkane® 365/277. The reaction mechanism was investigated with the ^{19}F NMR analysis.

論文審査結果の要旨

The initial report of SF_5-arenes appeared in the 1960s, but SF_5-group chemistry remained a "sleeping beauty" for the first 40 years. The SF_5 group, reasonably referred to as the "super-trifluoromethyl group", with intrinsically superior physicochemical properties, is currently being deployed to alter the physicochemical properties of drug-like molecules, while the application of SF_5-containing compounds is largely limited due to the lack of synthetic accessibility. This thesis describes our investigation in the preparation of SF_5 group containing compounds. We have developed the first general method for the synthesis of *m*-and *p*-SF_5-pyridines and functionalization of SF_5-pyridines by nucleophilic aromatic substitution reactions. Later, we disclosed the Cl-F exchange reaction of electron-deficient (hetero)arene-SF_4Cl could be successfully initiated in high yields through the use of IF_5 inhibiting a major side reaction of C-S bond cleavage. Finally, a novel approach for the silver-mediated self-immolative Cl-F exchange fluorination of arylsulfur chlorotetrafluorides to arylsulfur pentafluorides was achieved by a unique self-immolative fashion.

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In chapter 5, summary of the thesis was described.

以上のように，本論文ではペンタフルオロスルファニル化合物の新合成手法の開発に成功した。これらは，3編の有審査論文（うち，第1著者2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。