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学位の種類	博士（ナノメディシン科学）
学位記番号	博第1130号
学位授与の日付	平成30年3月26日
学位授与の条件	学位規則第４条第１項該当　課程博士
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.