Electrochemical Fluoroalkylation of Arenes and Heteroarenes Catalyzed by a Hydrophobic Vitamin B12

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論文名: Electrochemical Fluoroalkylation of Arenes and Heteroarenes
Catalyzed by a Hydrophobic Vitamin B<sub>12</sub>
ビタミン B<sub>12</sub>誘導体を触媒とするアレーンとヘテロアレーンに対する
電解フルオロアルキル化反応

区 分 :甲

## 論文内容の要旨

This thesis describes a straightforward methodology to demonstrate the radical difluoroalkylation, trifluoromethylation and perfluoroalkylation of aromatic compounds catalyzed by a Hydrophobic Vitamin  $B_{12}$  [Co(II)7C1ester]ClO4 (1) via an electrochemical technique.

**Chapter one** introduces the history and significance of fluorine in organic chemistry, and details the effect that substitution of a  $CF_3$  group can have on the properties of organic molecules and its many applications in fields ranging from pharmaceuticals to materials sciences. The exploration of a versatile fluoroalkylation reagents and methods to incorporate various fluoroalkyl groups are also described for the syntheses of bioactive fluoroalkylated compound. Brief history, general functions and synthesis of various model complexes of Vitamin  $B_{12}$  has also been discussed here.

**Chapter two** demonstrates the electrochemical trifluoromethylation and perfluoroalkylation of aromatic compounds mediated by a Vitamin B<sub>12</sub> derivative as a cobalt-based catalyst. The Co(I) species of a Vitamin B<sub>12</sub> derivative, prepared by controlled-potential electrolysis at -0.8 V vs. Ag/AgCl in methanol, reacted with R<sub>f</sub> (R<sub>f</sub> = CF<sub>3</sub>, n-C<sub>3</sub>F<sub>7</sub>, n-C<sub>4</sub>F<sub>9</sub>, n-C<sub>8</sub>F<sub>17</sub> and n-C<sub>10</sub>F<sub>21</sub>) to form a Co-R<sub>f</sub> complex. This complex released an R<sub>f</sub> radical under visible light irradiation, which then reacted directly with non-activated (hetero)arenes to form the desired fluoroalkylated molecules through direct C-H functionalization.

**Chapter three** describes the synthesis of atom economical difluoro-alkylated arene and (hetero)arene catalyzed by a Vitamin  $B_{12}$  derivative employing readily available reagent bromodifluoroacetate (Br-CF<sub>2</sub>COOEt) as a CF<sub>2</sub>- source through direct C-H functionalization. Different aspects of these reaction such as radical trapping experiment, catalyst concentration, reaction potential, substrate scope and solvent effects are discussed. The new protocol provides a much cheaper, mild and efficient way to difluoro, trifluoro and perfluoroalkylated organic compounds with the strategy outlined in **Scheme 1**.



[ $R_f X = C_3 F_7 I$ ,  $C_4 F_9 I$ ,  $C_8 F_{11} I$ ,  $C_{10} F_{21} I$  and  $Br \cdot CF_2 COOEt$ ]

Scheme 1 Proposed electro-catalytic cycles of radical fluoroalkylation of aromatic compounds mediated by  $[Co(II)7C_{1}ester]ClO_{4}(1)$ 

**Chapter four** reports the synthesis of Cobalt-CF<sub>3</sub> complex and describes the investigation of photolytic cleavage of Co-C bond in trifluoromethylated Vitamin  $B_{12}$  complex. Furthermore, a preliminary mechanistic study of fluoroalkylated complex mediated by a Vitamin  $B_{12}$  derivative in organic media is also reported.