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# Selective Transformations of Aromatic Trifluoromethyl Groups

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**ABSTRACT**

**The trifluoromethyl group is robust, hydrophobic, and electron-withdrawing. A wide range of molecules bearing trifluoromethyl groups have thus played crucial roles in the organic synthesis of a wide range of compounds. Nonetheless, despite vigorous studies on trifluoromethyl compounds, selective transformations of the C–F bond of trifluoromethyl groups remain challenging. I recently accomplished selective transformations of the C–F bond of aromatic trifluoromethyl groups under mild conditions. In particular, transformations of a single C–F bond of o-hydrosilyl-substituted benzotrifluorides have been achieved. I have also developed an efficient synthetic method for diaryl ketones via C–F cleavages of benzodifluorides**

**Keywords: Trifluoromethyl group, C–F bond, Silyl cations, Difluoromethylenes, Carbonyl compounds**

## INTRODUCTION

The trifluoromethyl group is a fundamental functional group in organic chemistry (**Fig. 1A**). The $CF_3$ group has for example played significant roles in the development of bioactive compounds owing to its uniquely robust and hydrophobic nature derived from its strong C–F bonds (**Fig. 1B**).Since fluorine is the most electro-negative element, $CF_3$ groups have a significant electron-withdrawing nature. The introduction of $_{CF3}$ groups into aromatic compounds thus significantly affects the electronic properties of the compounds, which is crucial in the development of organic electronic materials and organocatalysts.

The electron-withdrawing nature of aromatic $CF_3$ groups enables selective deprotonation at the orthoposition in synthetic chemistry, but the potential of benzotrifluorides in synthetic organic chemistry remains limited due to difficulties in the selective transformations of $CF_3$ groups. Aromatic difluoromethylenes are similar to benzotirifluorides and play a significant role in pharmaceuticals, but progress in their utilization has been slow due to the lack of information regarding the synthesis of difluoromethylenes.

Various efficient methods for installing $CF_3$ groups have been developed recently based on rapid improvements in organometallic chemistry. Single transformations of $CF_3$ groups can support the efficient synthesis of a broad range of difluoromethylenes, although such transformations require harsh conditions due to the strong C–F bonds. Transformations of $CF_3$ groups may result in further, facile C–F bond cleavages of CF2 moieties due to the Iaker C–F bonds, leading to the cleavage of all three C–F bonds (**Fig. 1C**).[3,4]

For example, in 2008, Ozerov and coworkers reported reduction of the $CF_3$ group of perfluorotoluene under mild conditions via the generation of a silyl cation bearing a carborane moiety as a counterion, and all three C–F bonds of the $CF_3$ group Ire reduced (**Fig. 1D**).[3a] Difficult selective transformations of the $CF_3$ group and the overreactions of difluoromethylenes has hindered exploration of synthetic chemistry strategies using the $CF_3$ group as a one-carbon unit.[5]

I recently found that selective transformations of the aromatic CF3 group can proceed under mild conditions (**Fig. 2**). Indeed, 1) difluoromethylene syntheses through the activation of ortho-hydrosilyl groups (**Fig. 2A**)6 and 2) ketone syntheses via arylation and carbonyl formation of CF3 groups (**Fig. 2B**)7 have been developed. This alloId us to demonstrate selective C–F transformations. These methods easily enabled us to expand the diversity of accessible products from simple starting materials in short steps. Herein, I summarize our recent achievements for C–F transformations of the CF3 group.

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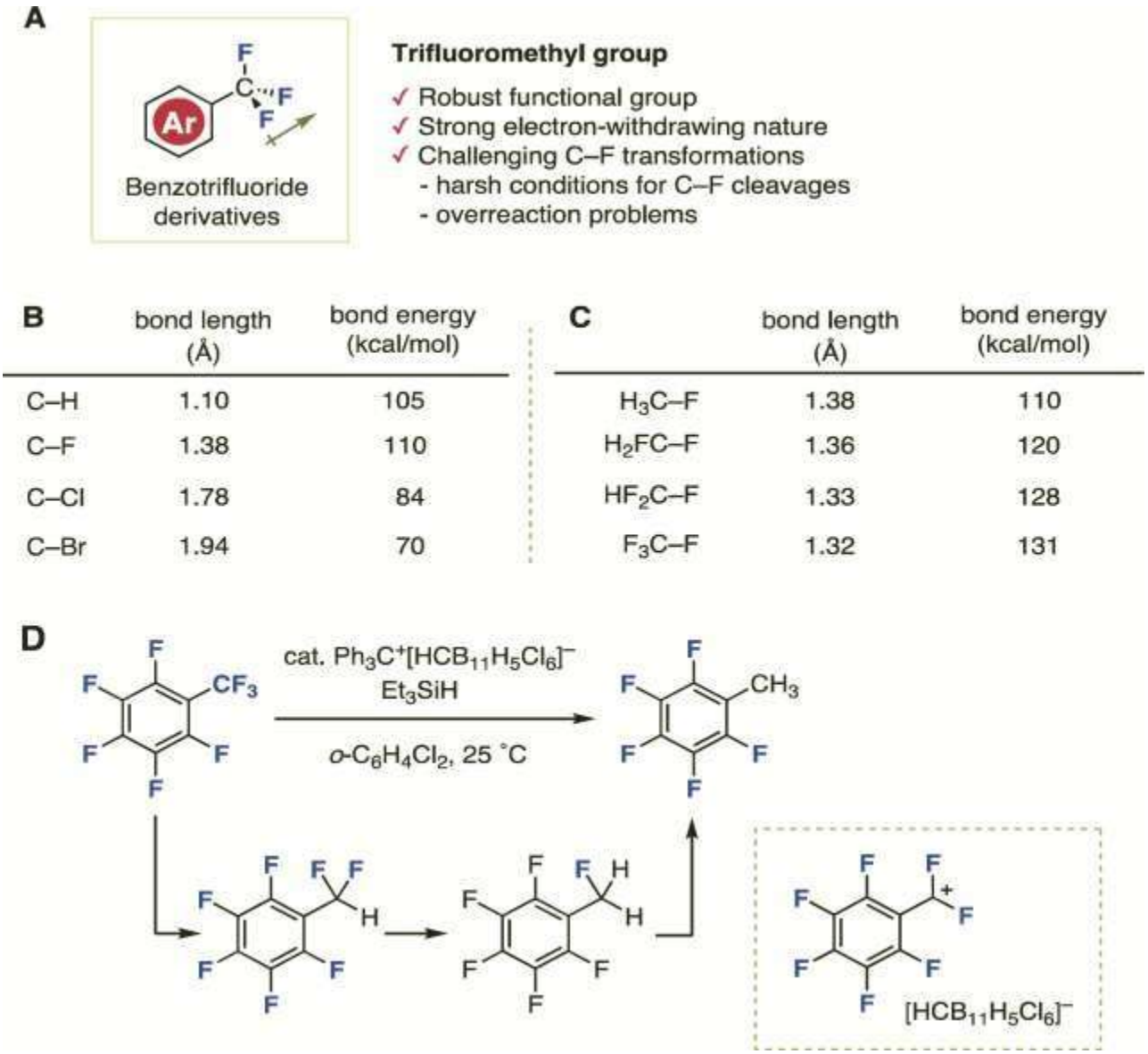


| B | bond length (Å) | bond energy (kcal/mol) |
|---|---|---|
| C–H | 1.10 | 105 |
| C–F | 1.38 | 110 |
| C–Cl | 1.78 | 84 |
| C–Br | 1.94 | 70 |

| C | bond length (Å) | bond energy (kcal/mol) |
|---|---|---|
| $H_3C–F$ | 1.38 | 110 |
| $H_2FC–F$ | 1.36 | 120 |
| $HF_2C–F$ | 1.33 | 128 |
| $F_3C–F$ | 1.32 | 131 |

**Figure 1. (A) Benzotrifluorides. (B) Carbon–hydrogen and carbon–halogen bonds. (C) Carbon–fluorine bonds. (D) Transformation of C–F bonds.**

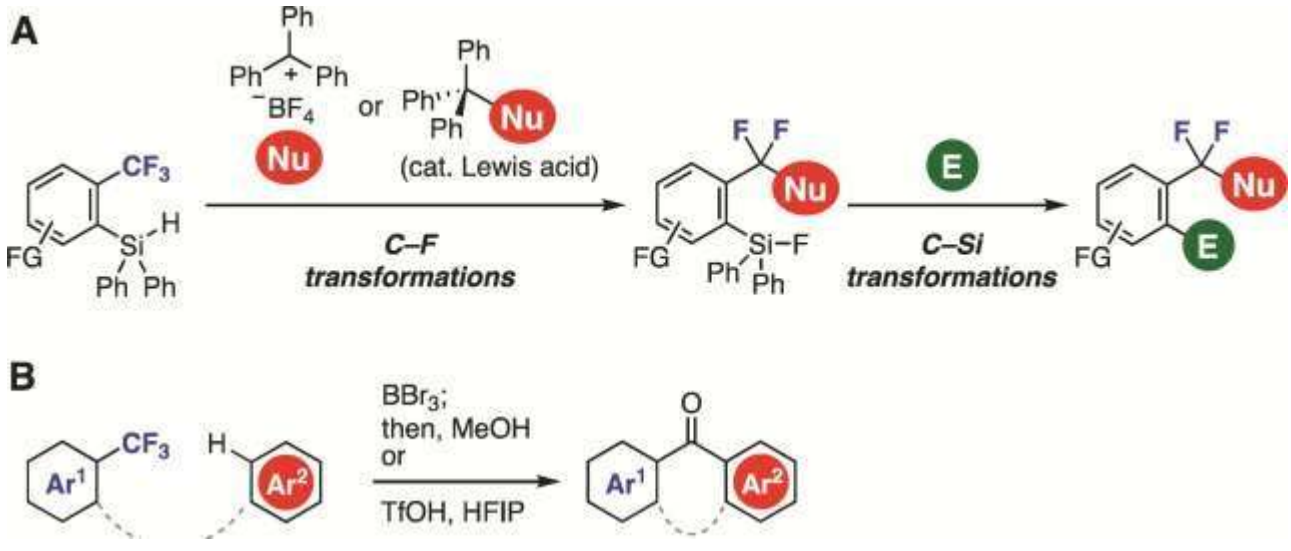


**Figure 2. (A) Difluoromethylene synthesis. (B) Diaryl ketone synthesis.**

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**2. Selective transformations of trifluoromethyl groups by ortho-hydrosilyl Groups**

**2-1. Monoallylation of trifluoromethyl groups6a**

The C–F transformation is challenging due to the robustness of trifluoromethyl groups, in which overreactions by further C–F transformations take place easily. I addressed this issue by designing a new reaction utilizing an ortho-hydrosilyl group of benzotrifluorides. Installation of the "dual-use" silyl group enabled us to achieve difluoromethylene synthesis from benzotrifluorides since 1) hydrosilyl groups can be used as precursors to generate silyl cations for C–F cleavage and 2) the resulting fluorosilyl group can be used in various transformations due to smooth activation with a base (**Fig. 3A**). I conceived that treatment of o-hydrosilyl Lsubstituted benzotrifluorides with a trityl cation supports C–F transformations via generation of a silyl cation by hydride abstraction from the hydrosilyl group, fluoride abstraction from a neighboring trifluoromethyl group, and nucleophilic attack with nucleophiles. The resulting fluorosilyl group can be activated with bases owing to the electro-negative fluoro group, allowing us to achieve a wide range of C–Si bond transformations. Thus, selective transformations of various difluoromethylenes can be accomplished from simple benzotrifluorides, nucleophiles, and electrophiles in two steps.

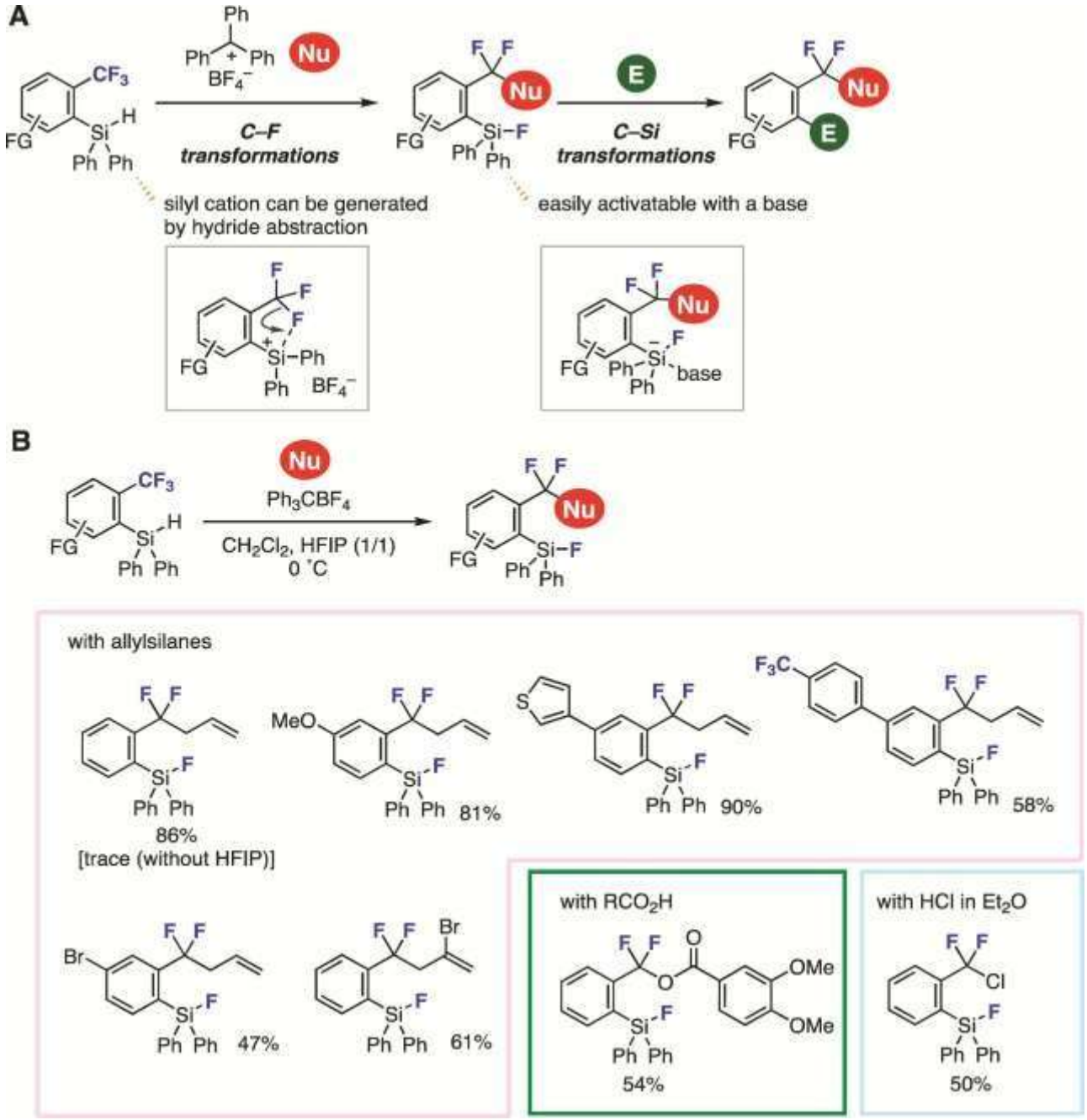


**Figure 3. (A) C–F transformations using the ortho-hydrosilyl group (B) Examples of single C–F transformations.**

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The desired C–F transformations Ire challenging due to the unstable silyl cation intermediates. I succeeded in the single C – Fallylation of o-diphenylsilyl-substituted benzotrifluorides by using a trityl cation in the presence of allylsilanes (**Fig. 3B**). The key to this success was the choice of solvents: dichloromethane and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP),10 which significantly stabilized the unstable cationic intermediates. Of note, no side products arising from further C–F transformations Ire observed in this reaction. I succeeded in the synthesis of various monoallylated products without damaging a range of functional groups, as Ill as achieving C–F carboxylation and chlorination. The transformations of fluorosilyl groups are described in section 2-4.

**2-2. Single thiolation of trifluoromethyl groups using all-in-one reagents6b**

Treatment of o-(diphenylsilyl)benzotrifluoride with a trityl cation in the presence of 4-methoxybenzenethiol afforded a trithiolated product in high yield through further thiolation of monothiolated product (**Fig. 4A**, upper). To solve this problem, I designed a reaction via the activation of trityl sulfides11 with Lewis acid catalysts (**Fig. 4B**). The activation of trityl sulphides generating thiolate ions and trityl cations would result in the single thiolation of benzotrifluorides since the generation of HBF4 can be prevented in this system using trityl sulfides instead of thiols. Indeed, treatment of o-(diphenylsilyl)benzotrifluorides with a catalytic amount of $Yb(OTf)_3$ in the presence of trityl sulphides provided the desired monothiolated product in good yield (**Fig. 4A**, loIr), where trithiolated product by overreactions through further C–F cleavage was not detected. I clarified that trityl cation was generated in equilibrium by treating trityl sulfides with a catalytic amount of $Yb(OTf)_3$. I accomplished the synthesis of diverse difluorobenzyl sulfides by the single thiolation of o-silylbenzotrifluorides.

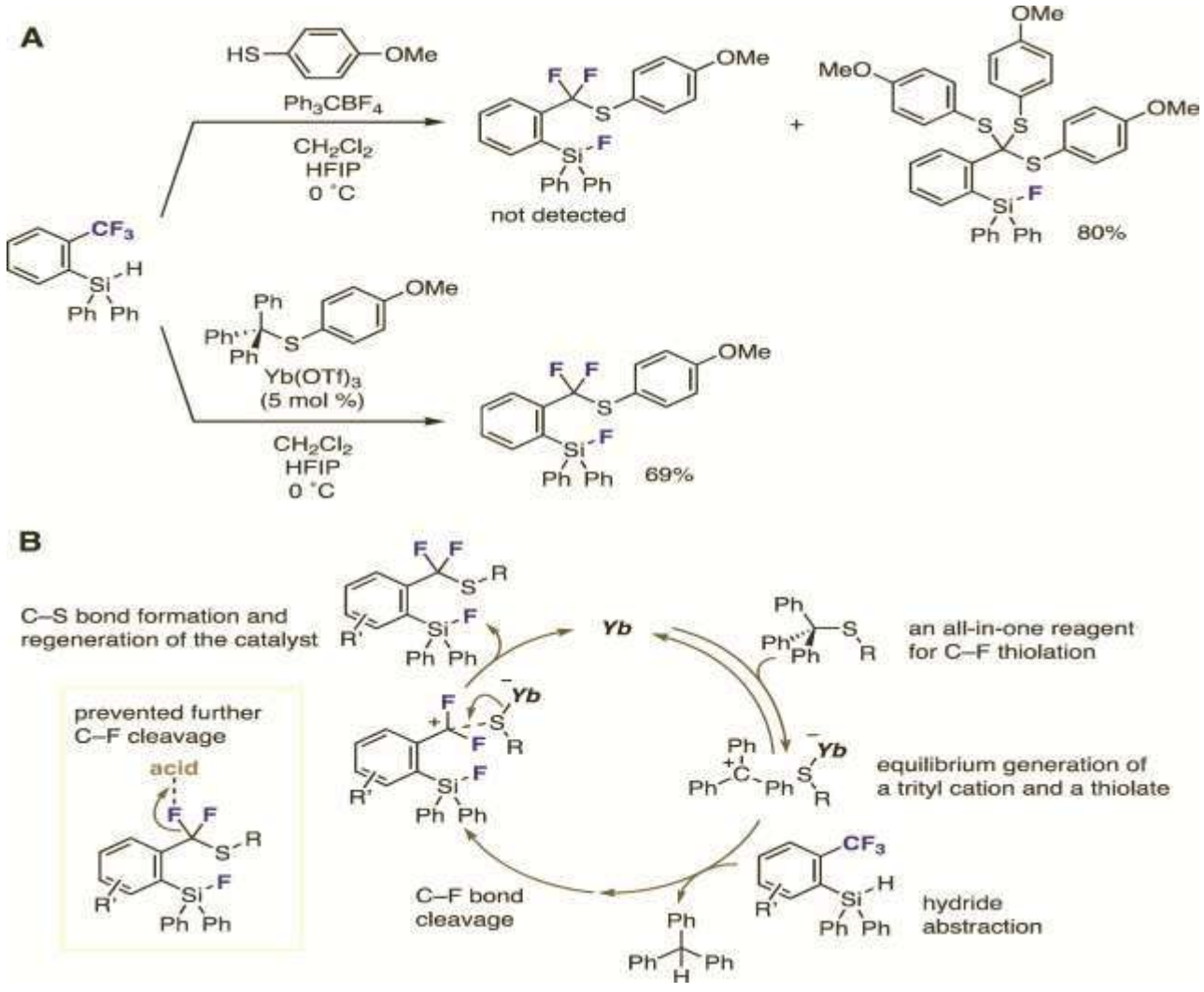


**Figure 4. (A) Thiolations of o-(diphenylsilyl)benzotrifluoride. (B) Plausible mechanism.**

**2-3. Single chlorination of trifluoromethyl groups using all-in-one reagents6c**

Single thiolation of benzotrifluorides required Lewis acid catalysts due to the C–S bond strength of trityl sulfides. In contrast, treatment of o-(diphenylsilyl) benzotrifluoride with trityl chloride in chlorobenzene and HFIP resulted in the single C–F chlorination without catalysts (**Fig. 5A**). A wide variety of difluoromethylenes Ire synthesized without

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further C–F transformations (**Fig. 5B**). I also accomplished single bromination and thiocyanation of o-silylbenzotrifluorides. The resulting α,α-difluorobenzyl chlorides are useful synthetic intermediates for diverse benzodifluorides by various transformations.12 While synthesizable α,α- difluorobenzyl chlorides by conventional methods Ire strictly limited, our method enabled us to prepare a wide variety of highly functionalized α,α-difluorobenzyl chlorides. The refore , this study will serve in organofluorine chemistry. Transformations of the chloro group are shown in section 2-4.

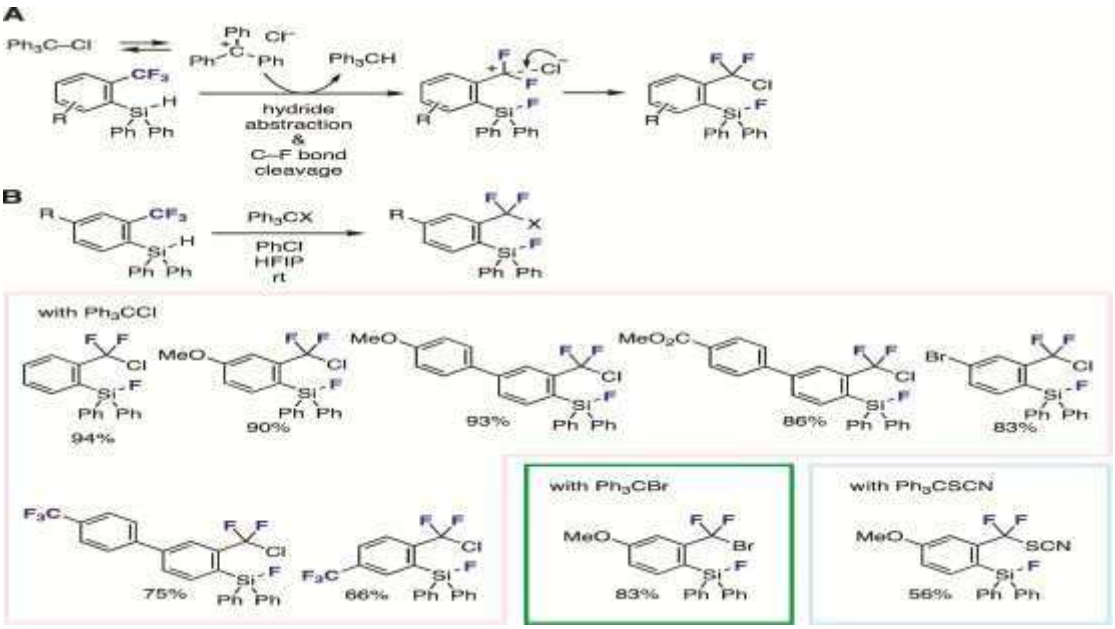


**Figure 5. (A) Single chlorination of benzotrifluorides. (B) Product examples.**

**2-4. Difluoromethylene synthesis by C–Si transformations6a–6c**

Since silyl groups bearing electron-negative atoms can be activated easily with bases, I succeeded in installing a wide variety of functional groups by C–Si transformations (**Fig. 6**). For example, desilylprotonation of o-fluorosilyl-substituted benzodifluorides with tetrabutylammonium fluoride without damaging difluoromethylene moieties. I accomplished C–Si arylation when performing palladium-catalyzed Hiyama cross-coupling9 of o-fluorosilyl-substituted benzodifluorides with aryl iodides. In contrast, no reaction proceeded when using hydrosilanes instead of fluorosilanes owing to the difficult activation with bases. In addition, desilylhalogenations Ire achieved by treatment of fluorosilanes with N-halosuccinimides in the presence of silver fluoride.13 These C–Si transformations alloId us to synthesize difluoromethylenes having a wide variety of functional groups at the ortho-position. These results clearly show that the "dual-use" silyl groups of benzotrifluorides enabled not only selective C–F transformations but also diversifications of products by further C–Si transformations.

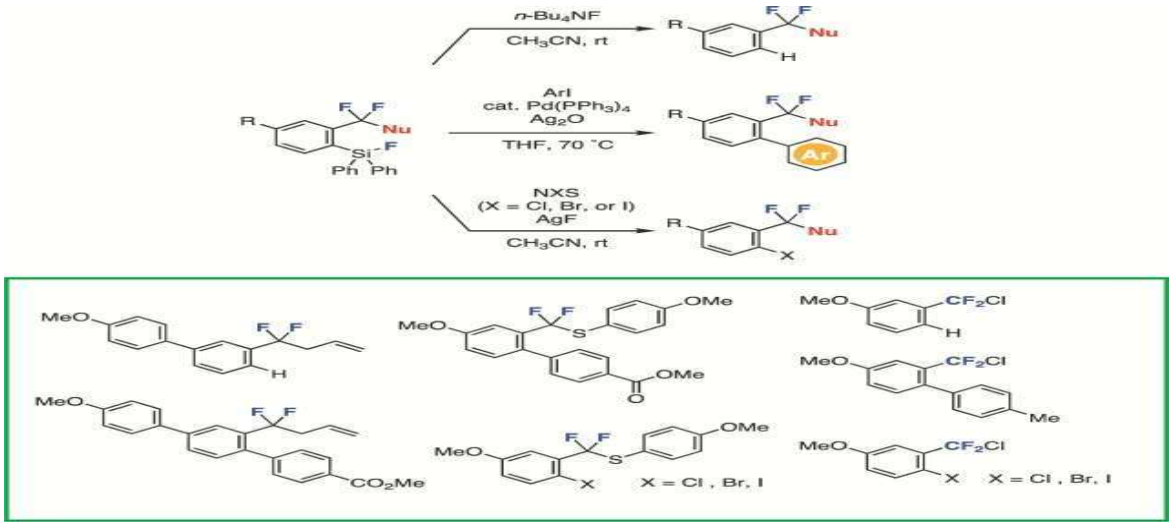


**Figure 6. Transformations of fluorosilyl groups (NXS = N-halosuccimide (X = Cl, Br, I))**

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Good transformability of α,α-difluorobenzyl chlorides alloId us to synthesize diverse organofluorines through single C–F chlorination of benzotrifluorides (**Fig. 7**). For instance, after the C–F monochlorination of o (diphenylsilyl) benzotrifluoride, desilylbromination was achieved without the purification of the reaction mixture of intermediates (**Fig. 7A**). I also succeeded in the synthesis of various difluorobenzyl ethers by substitution of chlorides with phenols under basic conditions (**Fig. 7B**). Radical C–C formation was accomplished by treatment of difluorobenzyl fluorides with samarium iodide in the presence of styrene as a radical acceptor (**Fig. 7C**). Studies on transformations of α,α-difluorobenzyl chlorides Ire immature and their contribution to synthetic chemistry was quite limited due to the poor accessibility before our studies. Contrastingly, I found that various transformations of α,α-difluorobenzyl chlorides obviously serve in the organofluorine synthesis.

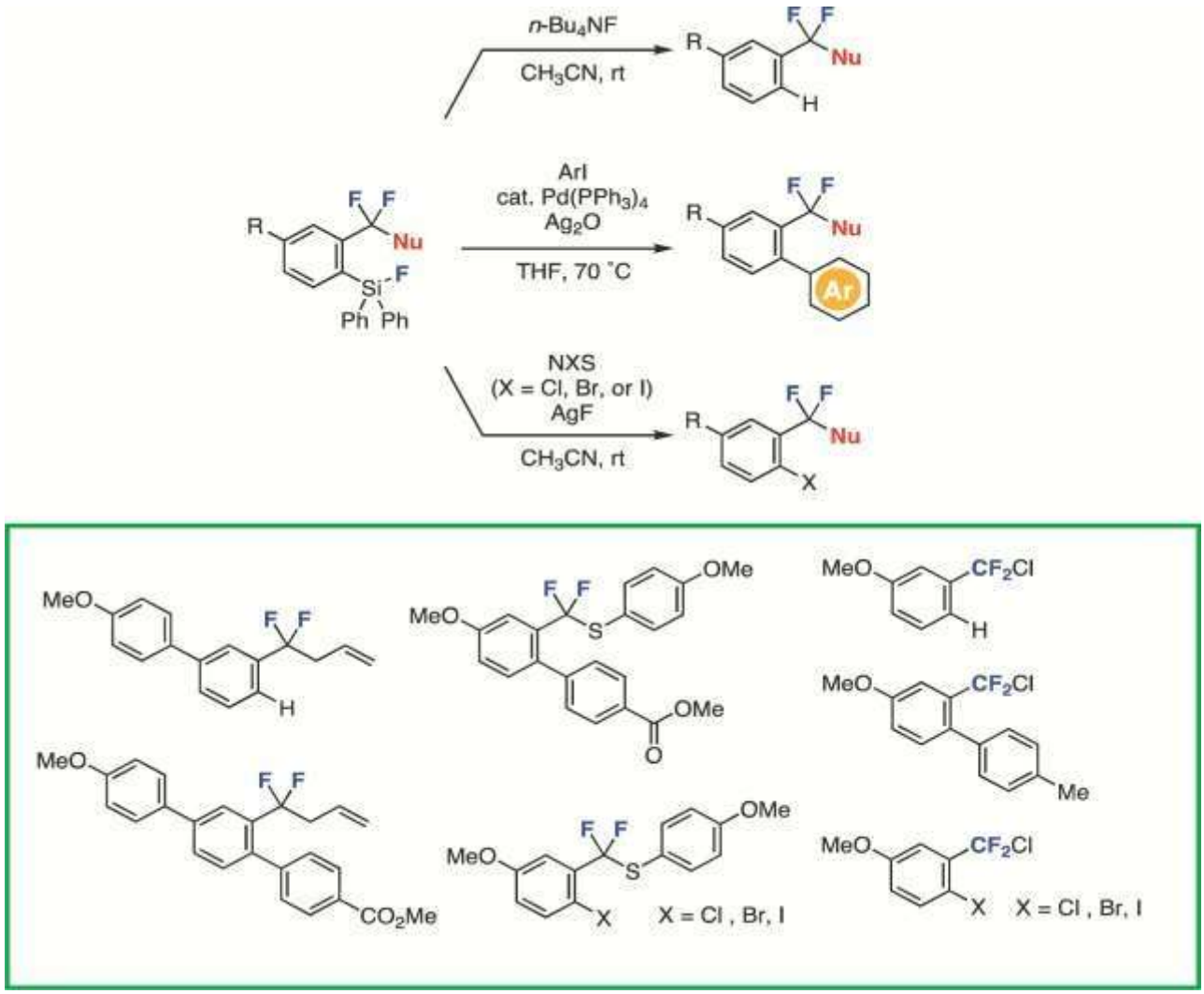


**Figure 7. (A) Difluorobenzyl chloride synthesis. (B) Difluorobenzyl ether synthesis. (C) Radical addition using difluorobenzyl chloride. (DMSO = dimethyl sulfoxide; HMPA = hexamethylphosphoric triamide; TMEDA = N,N,N',N'-tetramethylethylenediamine)**

**2-5. Sequential transformations via reduction of fluorosilyl groups6d**

I achieved the preparation of highly functionalized benzyl fluorides by the reduction of fluorosilyl group to reproduce the hydrosilyl group and following selective C–F transformations (**Fig. 8A**). Treatment of fluorosilanes with lithium aluminum hydride afforded hydrosilanes leaving difluoromethylene moieties untouched (**Fig. 8B**). Then, a single C–F transformation of the difluoromethylene moiety in the resulting hydrosilanes took place triggered by the second generation of a silyl cation (**Fig. 8C**). Indeed, treatment of difluoromethylenes with LAH in THF at 0 °C provided the corresponding hydrosilanes in high yields. When o-hydrosilylsubstituted difluoromethylenes Ire treated with trityl chloride, single chlorination of difluoromethylenes took place smoothly (**Fig. 8D**). I also succeeded in the synthesis of fluorobutadienes by desilylbromination of the fluorosilyl group and subsequent elimination with a base. Thus, I have developed a new method to prepare highly functionalized benzyl fluorides via the reduction of fluorosilyl group to regenerate hydrosilyl group and following single C–F transformations.

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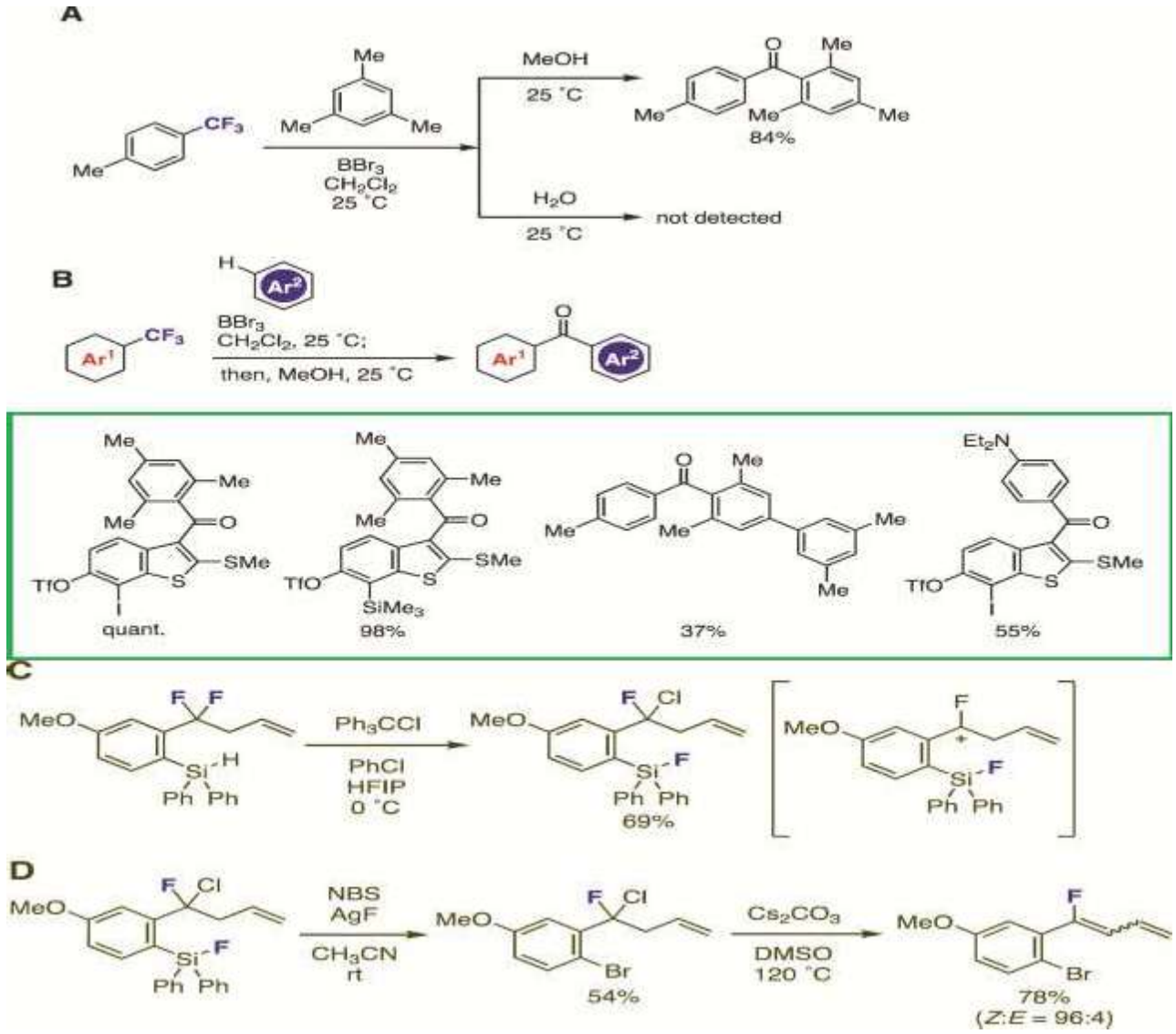


**Figure 8. (A) Benzyl fluoride synthesis through regeneration of hydrosilyl group. (B) Reduction of fluorosilyl group. (C) Single C–F chlorination. (D) Fluorobutadiene synthesis.**

### 3. Synthesis of carbonyl compounds by C–F transformations of trifluoromethyl Group

#### 3-1. Ketone synthesis using boron tribromide7a

Transformations of trifluoromethyl groups under mild conditions would allow us to synthesize diverse aromatic compounds having various functional groups. It is worth noting that the synthesis of benzotrifluoride derivatives can be performed under harsh conditions due to the robustness of the trifluoromethyl group. For example, ortho-deprotonation of benzotrifluorides enables us to synthesize various derivatives with a wide range of electrophiles. Thus, transformations utilizing trifluoromethyl group as a one-carbon unit will significantly contribute to the synthetic chemistry, which is advantageous over nucleophile-susceptible one-carbon units such as esters.

I have developed a facile method to synthesize ketones by electrophilic aromatic substitution and formation of carbonyl group via C–F cleavage using boron tribromide (**Fig. 9A**, upper). Indeed, the treatment of benzotrifluorides in dichloromethane with boron tribromide in the presence of arenes including mesitylene folloId by the addition of methanol, furnished benzophenone derivatives in good yields. In contrast, C–C bond formation did not take place before the addition of methanol, in which the formation of the tribromomethyl group from the trifluoromethyl group proceeded.15 When using water instead of methanol, the desired ketone was not observed (**Fig. 9A**, loIr). These results show that C–C bond formation was realized through the activation with Lewis acids generated in situ from boron tribromide and methanol. Selective transformations of trifluoromethyl group Ire accomplished without damaging highly reactive functional groups by virtue of the mild reactivity of boron tribromide (**Fig. 9B**). It is worth noting that I succeeded in the efficient arylation of trifluoromethyl group via C–F cleavages keeping triflusilyl, iodo, triflyloxy, and thio groups, which Ire reactive with acids, bases, transition metals, oxidants, etc.

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I achieved the efficient preparation of cyclic ketones such as thioxanthones via intramolecular arylation (**Fig. 9C**). Of note, it is easy to achieve various functionalizations through selective lithiation at the 2-position of 3 bromobenzotrifluoride. Indeed, the selective deprotonation folloId by arylthiolation and subsequent cyclization through C–F cleavages proceeded smoothly to afford a broad range of thioxanthones in good yields.

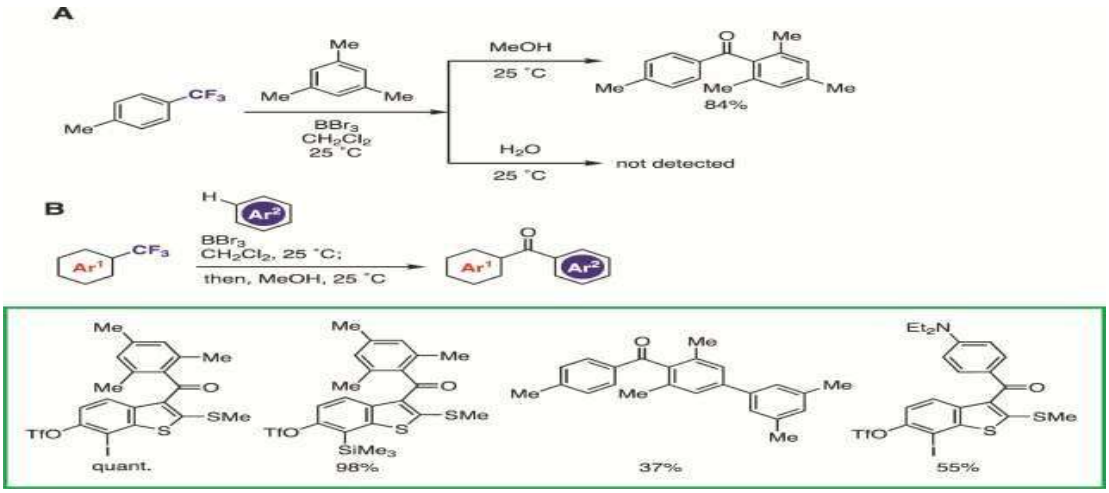


**Figure 9. (A) Diaryl ketone synthesis. (B) Product examples. (C) Thioxanthone synthesis**

**3-2. Cyclic ketone synthesis by cross-coupling and C–F transformation7b**

I have developed an efficient method to synthesize various cyclic ketones through cross-coupling reactions and following C–F arylation with the carbonyl formation from o-bromo- or o-iodobenzotrifluorides (**Fig. 10A**). Indeed, after arylation or aryloxylation at the bromo or iodo group, treatment of the resulting benzotrifluoride derivatives in HFIP with trifluoromethanesuofonic acid (TfOH)16 furnished various cyclic ketones in high yields (**Fig. 10B** and **10C**). It is worthy to note that I succeeded in the dimethoxyfluorenone synthesis from 3-methoxybenzotrifluoride via the selective deprotonation at 2-position, iodination, Suzuki–Miyaura cross-coupling, and ketone synthesis using TfOH in HFIP, where the corresponding ketone was obtained in good yield without purification of the intermediate.

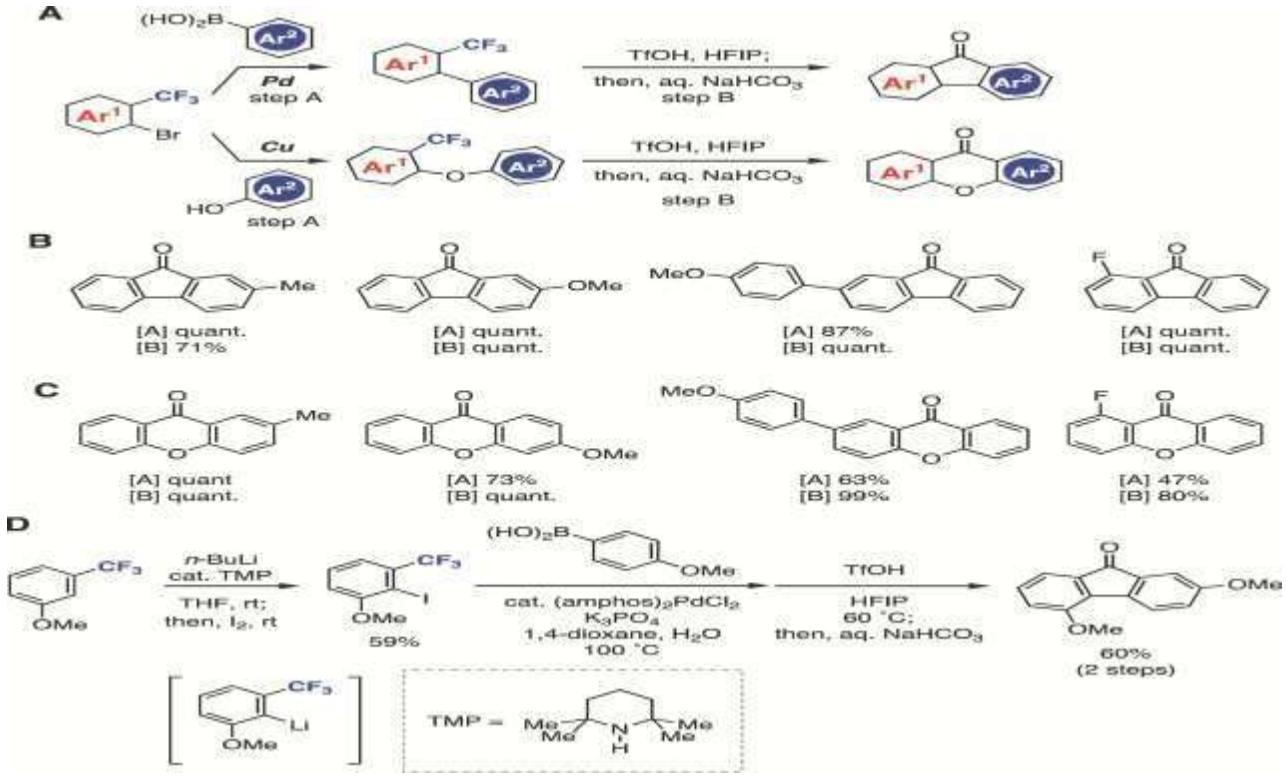


**Figure 10. (A) Synthesis of fluorenones and xanthones. (B) Examples of fluorenones. (C) Examples of xanthones. (D) Fluorenone synthesis from 3-methoxybenzotrifluoride**

## CONCLUSION

I have developed synthetic methods using the trifluoromethyl group. Although the trifluoromethyl group is robust under various reaction conditions, selective C–F transformations of aromatic trifluoromethyl groups can be accomplished without damaging highly reactive functional groups on the basis of proper design of substrates or choice of reagents. At the beginning of our studies, the selective C–F transformation was not a popular topic.

However, diverse chemists are recently gaining attention to C–F transformations as hot topics.17–20 Future studies such as the development of transformations based on the features of the trifluoromethyl group and synthetic methods using organofluorines which can be prepared by our methods will lead to the great advance of synthetic methodologies utilizing one-carbon units having fluorine atoms such as trifluoromethyl groups.

I clarified the reactivities of aromatic molecules bearing trifluoromethyl groups through studies on the development of novel reactions as described above. Our further studies on not only new transformations using popular functional groups but also developing new reactions and new reagents based on disclosing unpopular functional groups will expand the potential of organic chemistry.

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