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# Argentination of Fluoroform: Preparation of Stable $AgCF_3$ Solution with Diverse Reactivities

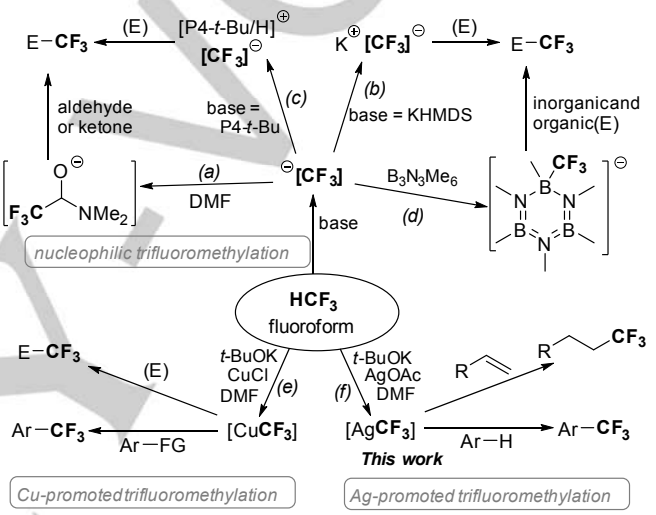
Jia-Xiang Xiang, Yao Ouyang, Xiu-Hua Xu, and Feng-Ling Qing*

**Abstract:** The transformation of large-volume industrial by-product and stable greenhouse gas fluoroform ($HCF_3$) to useful products has recently received significant attention. Herein, we disclose a simple and scalable preparation of $AgCF_3$ by treatment of $HCF_3$ with *t*-BuOK and AgOAc. The reactivity of the $HCF_3$-derived $AgCF_3$ has been demonstrated by hydrotrifluoromethylation of alkenes and C–H trifluoromethylation of (hetero)arenes. This work not only provides a new avenue for the utilization of $HCF_3$, but also presents a reliable and easy-to-execute synthesis of the relatively stable $AgCF_3$ solution.

Fluoroform ($HCF_3$) is a large-volume by-product from fluoropolymer manufacturing and has high greenhouse effect.[1] The utilization of fluoroform as a feedstock for the preparation of valuable fluorinated compounds is a clearly preferred alternative to the destruction of fluoroform. Obviously, the application of fluoroform for trifluoromethylation reaction is a highly attractive and much-sought-after goal,[2] as it is the cheapest and most atom-economical but low reactivity $CF_3$ source.

The common strategy to use $HCF_3$ in trifluoromethylation reactions is based on deprotonation with strong bases. Several groups have reported the nucleophilic trifluoromethylation of carbonyl compounds with $HCF_3$ in the presence of electrogenerated bases or alkali metal bases in DMF (Scheme 1a).[3] The solvent DMF traps the *in situ* generated $CF_3$ anion, which easily decomposes to fluoride anion and difluorocarbene,[4] producing a reservoir of trifluoromethylating hemiaminolate species. Prakash (Scheme 1b)[5] and Shibata (Scheme 1c)[6] described the nucleophilic trifluoromethylation with $HCF_3$ in common organic solvents such as THF, ether, and toluene using KHMDS or P4-*t*-Bu respectively as the base. Very recently, Szymczak disclosed that hexamethylborazine ($B_3N_3Me_6$) could act as a suitable Lewis acid to stabilize $CF_3$ anion.[7] This $HCF_3$-derived borazine $CF_3^-$ adduct is highly nucleophilic and reacts with a broad variety of inorganic and organic electrophiles (Scheme 1d).

In 2011, Grushin discovered a methodologically different approach to activation of $HCF_3$ through direct cupration of $HCF_3$ with *t*-BuOK and CuCl in DMF (Scheme 1e).[8a] This $HCF_3$-derived $CuCF_3$ not only reacts with electrophiles, but also trifluoromethylates aryl halides, boronic acids, and diazonium salts.[8] Following Grushin's pioneering work, several groups further extended the application of $HCF_3$-derived $CuCF_3$ for Cu-promoted trifluoromethylation of a wider range of substrates.[9] Beside cupration of $HCF_3$, the direct metallation of $HCF_3$ with other metals (Zn,[10] Ir,[11] and Pd[12]) has also been reported. However, the synthetic applications of these metal-$CF_3$ complexes are limited.[10-12]




**Scheme 1.** Use of $HCF_3$ in Trifluoromethylation Reactions.

Recently, our group[13] and others[14,15] developed a series of Ag-promoted trifluoromethylation reactions, in which $AgCF_3$ was formed as the reactant[14] or reaction intermediate.[13,15] Due to the thermal and light sensitivity, normally $AgCF_3$ needs to be freshly prepared[14] or *in situ* generated[13,15] from $TMSCF_3$ and AgF. On the other hand, although the stable ligand-supported $AgCF_3$ complexes[14d,15b,16] are available, they are only used as transmetalating agents. Therefore, the synthesis of stable $AgCF_3$ with diverse reactivities is highly desirable. As part of our research interest in the development of trifluoromethylation reaction using cheap $CF_3$ sources,[17] herein we disclose a practical preparation of the stable $AgCF_3$ solution from simple and inexpensive materials $HCF_3$, *t*-BuOK, and AgOAc (Scheme 1f). The synthetic utility of the $HCF_3$-derived $AgCF_3$ is exemplified by hydrotrifluoromethylation of alkenes and C–H trifluoromethylation of (hetero)arenes. Notably, it is difficult to achieve these transformations directly from the $HCF_3$-derived $CuCF_3$.

Our investigation started with the preparation of $AgCF_3$ by treatment of excess of $HCF_3$ with *t*-BuOK in the presence of $Ag^I$ salts using DMF as the solvent (Table 1). The use of AgCl afforded the [$AgCF_3$] (resonates at $\delta$ = −20.7 ppm, d, $J(^{107/109}Ag\text{-}F)$ = 109.0/124.1 Hz)[14a,18] in 41% yield along with $[Ag(CF_3)_2]^-$ (resonates at $\delta$ = −25.4 ppm, d, $J(^{107/109}Ag\text{-}F)$ = 86.5/101.5 Hz)[14a,18] in 8% yield (entry 1). Then, other $Ag^I$ salts were screened to improve the yield of $AgCF_3$. Among all the $Ag^I$ salts

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(entries 2-6), AgOAc was optimal to afford $AgCF_3$ in highest yield (entry 5). Reducing the reaction time from 8 to 1 h further improved the yield (entry 7). The use of stoichiometric amount of $CF_3H$ also led to satisfactory yield (entry 8). Notably, this reaction can be easily scaled up to 40.0 mmol in 87% yield (entry 9).

***Table 1.*** Preparation of $AgCF_3$ from $HCF_3$ [a]

$HCF_3$ + Ag salt $\xrightarrow[DMF,\ rt]{t\text{-BuOK}}$ $[Ag\mathbf{CF_3}]$ + $[Ag(\mathbf{CF_3})_2]^-$

| Entry | Ag salt | Yield ($[Ag\mathbf{CF_3}]$, %)[b] | Yield ($[Ag(\mathbf{CF_3})_2]^-$, %)[b] |
|---|---|---|---|
| 1 | AgCl | 41 | 4 |
| 2 | AgBr | 20 | 28 |
| 3 | $AgNO_3$ | 0 | 22 |
| 4 | $AgBF_4$ | 0 | 23 |
| 5 | AgOAc | 59 | 12 |
| 6 | $AgOCOCF_3$ | 48 | 8 |
| 7[c] | AgOAc | 80 | 4 |
| 8[c,d] | AgOAc | 80 | 4 |
| 9[e] | AgOAc | 87 | 3 |

[a] Reaction conditions: $HCF_3$ (excess), Ag salt (0.2 mmol), *t*-BuOK (1.0 mmol), DMF (2.0 mL), $N_2$, rt, 8 h. [b] Yields determined by $^{19}F$ NMR spectroscopy using trifluorotoluene as an internal standard. [c] The reaction was performed for 1 h. [d] $HCF_3$ (0.2 mmol), *t*-BuOK (0.4 mmol). [e] $HCF_3$ (40.0 mmol), AgOAc (40.0 mmol), *t*-BuOK (80.0 mmol), DMF (40.0 mL), $N_2$, rt, 1 h.

Like the $HCF_3$-derived $CuCF_3$,[8a] $HCF_3$-derived $AgCF_3$ also exhibited high stability. The solution of $HCF_3$-derived $AgCF_3$ in DMF was stored under $N_2$ atmosphere in the refrigerator for months without noticeable decomposition. Even a solution of $AgCF_3$ in DMF (0.55 M) was placed under air at room temperature, only slow decomposition of $AgCF_3$ was detected (Table 2). Furthermore, the thermal stability of the $HCF_3$-derived $AgCF_3$ solution was probed. This solution was found to have reasonable stability at 60 °C for hours (Table 2).

***Table 2.*** Stability of $HCF_3$-derived $AgCF_3$ solution

| Entry | Time | in air at rt M ($[Ag\mathbf{CF_3}] + [Ag(\mathbf{CF_3})_2]^-$)[a] | under $N_2$ at 60 °C M ($[Ag\mathbf{CF_3}] + [Ag(\mathbf{CF_3})_2]^-$)[a] |
|---|---|---|---|
| 1 | 0 h | 0.53 + 0.02 | 0.53 + 0.02 |
| 2 | 4 h | 0.52 + 0.02 | 0.32 + 0.03 |
| 3 | 12 h | 0.50 + 0.02 | 0.25 + 0.02 |
| 4 | 24 h | 0.44 + 0.02 | 0.15 + 0.01 |
| 5 | 48 h | 0.41 + 0.02 | 0.08 + 0.01 |

[a] Concentrations determined by $^{19}F$ NMR spectroscopy using trifluorotoluene as an internal standard.

This $HCF_3$-derived $AgCF_3$ solution represents a rare example of stable $AgCF_3$ reagents. It is much more stable than the common $AgCF_3$ reagent prepared from $TMSCF_3$ and AgF in MeCN (Table 3, entries 1 and 2). When DMF was used as solvent instead of $CH_3CN$ for the formation of $AgCF_3$ from $TMSCF_3$ and AgF, the stability of $AgCF_3$ reagent was slightly improved, but still significantly lower than that of $HCF_3$-derived $AgCF_3$ solution (entry 3). Furthermore, the effect of additive on the stability of $AgCF_3$ generated from $TMSCF_3$ and AgF was investigated. Among these additives including KOAc, *t*-BuOK, and *t*-BuOH, it was found that *t*-BuOK was crucial to the stability of $AgCF_3$ (entries 4-6).

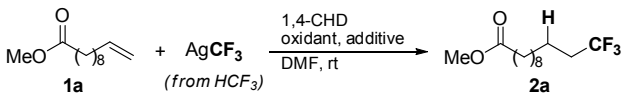
***Table 3.*** Comparison of $HCF_3$-derived $AgCF_3$ with those prepared from $TMSCF_3$

| Entry | Preparation of $Ag\mathbf{CF_3}$ | % remained in air at rt[a] | | | |
|---|---|---|---|---|---|
| | | 0 h | 4 h | 12 h | 24 h |
| 1 | $H\mathbf{CF_3}$ *t*-BuOK/AgOAc/DMF | 100 | 98 | 95 | 84 |
| 2 | $TMS\mathbf{CF_3}$ AgF/MeCN | 100 | 68 | 39 | trace |
| 3 | $TMS\mathbf{CF_3}$ AgF/DMF | 100 | 70 | 46 | trace |
| 4 | $TMS\mathbf{CF_3}$ AgF/DMF/KOAc | 100 | 76 | 66 | 18 |
| 5 | $TMS\mathbf{CF_3}$ AgF/DMF/*t*-BuOK | 100 | 83 | 73 | 53 |
| 6 | $TMS\mathbf{CF_3}$ AgF/DMF/*t*-BuOH | 100 | 74 | 11 | trace |

[a] Percentages determined by $^{19}F$ NMR spectroscopy using trifluorotoluene as an internal standard.

With the $HCF_3$-derived $AgCF_3$ in hand, the hydrotrifluoromethylation of alkenes was then examined using methyl undec-10-enoate (**1a**) as the model substrate.[19] The reaction of **1a** with a solution of $AgCF_3$ in DMF in the presence of 1,4-cyclohexadiene (1,4-CHD) failed to afford the desired product **2a** (Table 4, entry 1). As $HCF_3$-derived $AgCF_3$ is too stable to spontaneously collapse to form $CF_3$ radical, the extra oxidant was used to oxidize $AgCF_3$ to generate $CF_3$ radical. Accordingly, when $PhI(OAc)_2$ was added to the reaction mixture, the desired product **2a** was formed in 50% yield (entry 2). Switching the oxidant to $PhI(OCOCF_3)_2$ led to lower yield (entry 3). Subsequently, different additives including *N*- or *O*-containing donors were added to further improve the yield of **2a** (entries 4-9). Among them, HOAc was optimal to furnish **2a** in 85% yield (entry 7). The role of HOAc might be to activate *t*-BuOH- and/or DMF-coordinated $AgCF_3$ complex through ligand exchange.[9m,20]

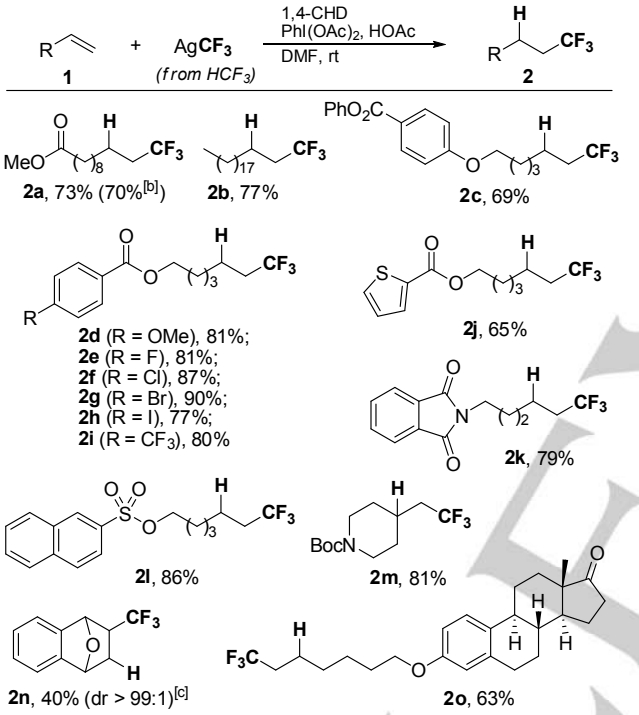
***Table 4.*** Optimization of reaction conditions for hydrotrifluoromethylation of alkene **1a**[a]




| Entry | Oxidant | Additive | Yield (%)[b] |
|---|---|---|---|
| 1 | — | — | 0 |
| 2 | $PhI(OAc)_2$ | — | 50 |
| 3 | $PhI(OCOCF_3)_2$ | — | 43 |
| 4 | $PhI(OAc)_2$ | pyridine | 42 |
| 5 | $PhI(OAc)_2$ | $NEt_3$ | 48 |
| 6 | $PhI(OAc)_2$ | *t*-BuOH | 60 |
| 7 | $PhI(OAc)_2$ | HOAc | 85 |
| 8 | $PhI(OAc)_2$ | $CF_3CO_2H$ | 70 |
| 9 | $PhI(OAc)_2$ | $CF_3SO_3H$ | 75 |

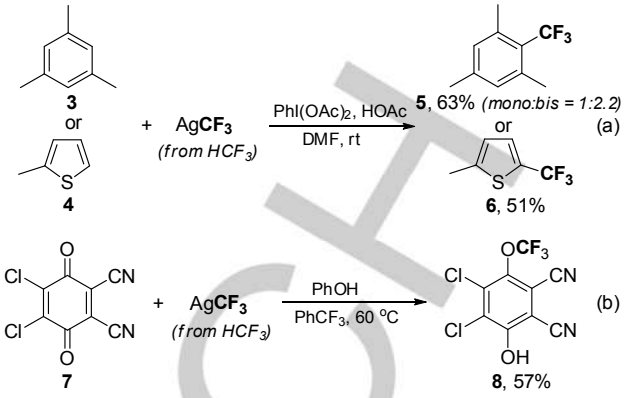
[a] Reaction conditions: **1a** (0.2 mmol), $AgCF_3$ (0.4 M, 2.0 mL, 0.8 mmol), 1,4-CHD (0.4 mmol), oxidant (0.8 mmol), additive (0.2 mmol), DMF (2.0 mL), $N_2$, rt, 12 h. [b] Yields determined by $^{19}F$ NMR spectroscopy using trifluorotoluene as an internal standard.

The scope of this oxidative hydrotrifluoromethylation was then investigated using $HCF_3$-derived $AgCF_3$ under optimized reaction conditions. As shown in Scheme 2, various alkenes were converted to the hydrotrifluoromethylated products in moderate to excellent yields. Interestingly, the reaction of **1a** was scaled up to 6.0 mmol with good efficiency. A wide range of functional groups, such as ether, ester, sulfonate, amide, and halogen atoms well tolerated under the reaction conditions. It should be noted that alkene **1j** bearing thienyl moiety was compatible with the reaction protocol. Furthermore, 1,1-disubstituted alkene **1m** delivered **2m** in 81% yield, whereas 1,2-disubstituted alkene **1n** furnished **2n** in 40% yield. The synthetic utility of this reaction was also demonstrated by late-stage hydrotrifluoromethylation of estrone derivative (**1o**).



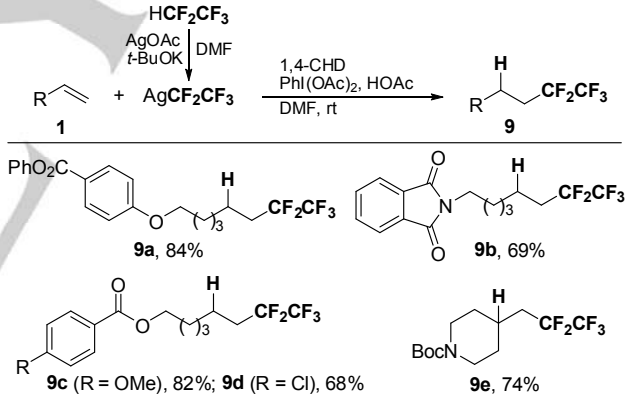

**Scheme 2.** Hydrotrifluoromethylation of alkenes with $AgCF_3$. Reaction conditions: **1** (0.6 mmol), $AgCF_3$ (0.4 M, 6.0 mL, 2.4 mmol), 1,4-CHD (1.2 mmol), $PhI(OAc)_2$ (2.4 mmol), HOAc (0.6 mmol), DMF (6.0 mL), $N_2$, rt, 12 h, isolated yields. [b] The reaction was performed on 6.0 mmol. [c] Diastereomeric ratio was determined by $^{19}F$ NMR analysis of the reaction mixture.

This $HCF_3$-derived $AgCF_3$ was applied to other types of trifluoromethylation reactions. For instance, the C–H trifluoromethylation of arene **3** and heteroarene **4** with $AgCF_3$ afforded trifluoromethylated products **5** and **6** in moderate yields (Scheme 3a). Furthermore, treatment of 2,3-dicyano-5,6-dichlorobenzoquinone (DDQ, **7**) with $AgCF_3$ using PhOH as a proton donor furnished 1,6-hydrotrifluoromethylated[21] product **8** in 57% yield (Scheme 3b). The 1,6-hydrotrifluoromethylation of quinones is previously unknown and might find applications for the preparation of novel 4-trifluoromethoxyphenols.




**Scheme 3.** Trifluoromethylation of (hetero)arenes and quinone with $AgCF_3$.

To extend the application of this protocol, $AgCF_2CF_3$ was prepared from $HCF_2CF_3$ (HFC-125, fire extinguishing agent) and applied to the hydropentafluoroethylation of alkenes (Scheme 4). Being different from the preparation of $AgCF_3$ along with formation of minor $[Ag(CF_3)_2]^-$ (Table 1), $[AgCF_2CF_3]$ was solely formed when $HCF_2CF_3$ was treated with *t*-BuOK and AgOAc.[22] The oxidative hydropentafluoroethylation of alkenes in the presence of $PhI(OAc)_2$, 1,4-CHD, and HOAc also proceeded efficiently to give the pentafluoroethylated products in moderate to excellent yields.[23]




**Scheme 4.** Hydropentafluoroethylation of alkenes with $AgCF_2CF_3$. Reaction conditions: **1** (0.6 mmol), $AgCF_2CF_3$ (0.4 M, 6.0 mL, 2.4 mmol), 1,4-CHD (1.2 mmol), $PhI(OAc)_2$ (2.4 mmol), HOAc (0.6 mmol), DMF (6.0 mL), $N_2$, rt, 12 h, isolated yields.

In conclusion, we have described a new protocol for the utilization of fluoroform through the transformation to the synthetically useful $AgCF_3$. The $HCF_3$-derived $AgCF_3$ solution exhibited unique stability and diverse reactivities. Furthermore, $HCF_2CF_3$ was also converted to $AgCF_2CF_3$ solution for the preparation of pentafluoroethylated products. Further developments of new applications of $R_fH$-derived $R_fAg$ are under investigation in our laboratory.

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**Keywords:** fluoroform • trifluoromethylation • alkene • silver • pentafluoroethylation

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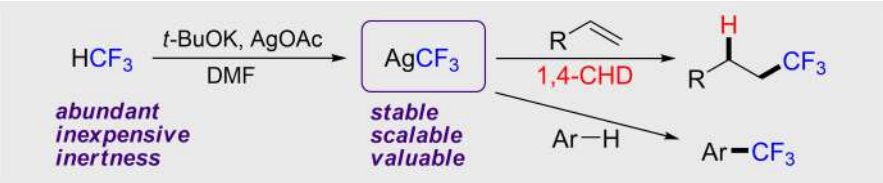
# COMMUNICATION




The direct argentination of fluoroform with *t*-BuOK and AgOAc in DMF provided a practical approach to $AgCF_3$. The $HCF_3$-derived $AgCF_3$ solution exhibited unique stability and diverse reactivities, such as the hydrotrifluoromethylation of alkenes and C–H trifluoromethylation of arenes.

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**Argentination of Fluoroform: Preparation of Stable $AgCF_3$ solution with Diverse Reactivities**