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Silver-Catalyzed C−H Trifluoromethylation of Arenes Using Trifluoroacetic Acid as the Trifluoromethylating Reagent

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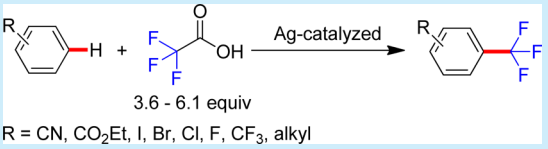
Supporting Information

ABSTRACT: Direct trifluoromethylation of arenes using TFA as the trifluoromethylating reagent was achieved with Ag as the catalyst. This reaction not only provides a new protocol for aryl C−H trifluoromethylation, but the generation of CF_3· from TFA may prove useful in other contexts and could potentially be extended to other trifluoromethylation reactions.



The incorporation of trifluoromethyl groups into organic molecules can endow them with unique and useful properties.[1] As a result, the trifluoromethyl group is an essential structural motif that is widely present in pharmaceuticals, agrochemicals, and materials.[2] Accordingly, the development of efficient trifluoromethylation methods has been the subject of extensive research.[3] Trifluoromethylarenes are among the most important and useful classes of trifluoromethylated organic molecules. Therefore, their synthesis has attracted considerable attention.[4] Direct aryl C−H trifluoromethylation, in particular, has been an active research topic in recent years,[5] and various catalytic reactions have been developed using transition metals, including Pd,[6] Cu,[7] and others.[8−11] Recently, radical trifluoromethylation has witnessed a resurgence of interest, and several synthetically useful reactions have been disclosed for introducing aryl trifluoromethyl groups.[12,13]

The rapid development of novel trifluoromethylation reactions has largely been driven by the discovery of new trifluoromethylating reagents.[14] Generally speaking, trifluoromethylating reagents can be divided into three classes as shown in Figure 1: (1) nucleophilic, (2) electrophilic, and (3) radical. It should be noted, however, that depending on the reaction conditions, these reagents can be converted in situ into different reactive trifluoromethyl species. While the availability of these reagents has enabled trifluoromethylation of a wide range of organic molecules, there remain drawbacks associated with their use. Many of the reagents in Figure 1 are expensive, toxic, or operationally inconvenient, and some are not commercially available or generate large quantities of chemical waste. Therefore, it is highly desirable to design new trifluoromethylating reagents without these drawbacks and develop reactions that efficiently transform abundant but underutilized trifluoromethyl sources.

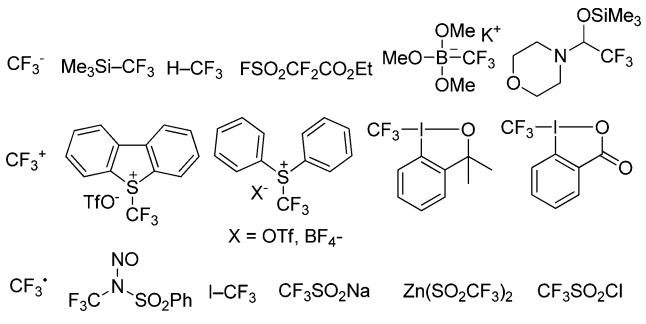


Figure 1. Common trifluoromethylating reagents.

In this respect, trifluoroacetic acid (TFA) has several attractive features. It is cheap and readily available.[15] CO_2 is the sole byproduct generated from TFA, which makes the reaction environmentally benign.[16] Notably, TFA has been successfully applied to the trifluoromethylation of aryl iodides and aryl bromides in the presence of catalytic or stoichiometric amounts of copper.[17]

Attracted to these potential advantages, we sought to investigate C−H trifluoromethylation of arenes using TFA. Very few reactions of this type have previously been reported, and they have required electrochemical[18] or photochemical conditions[19] or relied on the use of a stoichiometric amount of toxic XeF_2.[20] To the best of our knowledge, these reports are the only earlier examples for direct C−H trifluoromethylation of arenes with TFA as the CF_3 sources. We aimed to develop more generally useful trifluoromethylation methodology with TFA as the CF_3 source. To this end, herein we describe a silver-catalyzed C−H trifluoromethylation reaction of arenes using TFA as the trifluoromethylating reagent.

We first examined trifluoromethylation of pyridine with TFA under the standard Minisci reaction conditions.[21] Unfortunately, the reaction did not give any trifluoromethylated products. Gratifyingly, after extensively surveying reaction conditions, we found that terephthalonitrile could be trifluoromethylated with TFA in 17% yield under the conditions as shown in Table 1, entry 3. Surprisingly, the yield increased to 55% when there was a small opening in the flask and further improved to 81% including 21%

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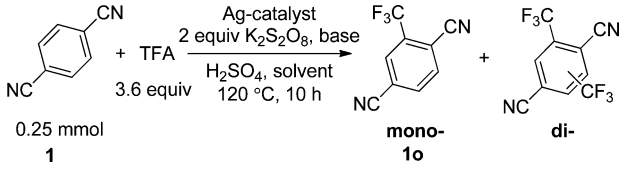
Table 1. Optimization of Trifluoromethylation Reaction



0.25 mmol **1** — **mono-1o** — **di-**

entry	catalyst (mol %)	base (equiv)	H_2SO_4 (equiv)	solvent (mL)	yield[a] (%)
1[b]	Ag_2CO_3 (40)	–	–	MeCN (0.4)	trace
2[b]	Ag_2CO_3 (40)	–	0.2	MeCN (0.4)	trace
3[b]	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	–	MeCN (0.4)	17
4	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	–	MeCN (0.4)	55 (di-:17)
5	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	MeCN (0.4)	56 (di-:8)
6	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	–	MeCN (0.9)	57 (di-:14)
7	**Ag_2CO_3 (40)**	**Na_2CO_3 (1.5)**	**0.5**	**MeCN (0.9)**	**81 (di-:21)**
8[b]	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	MeCN (0.2)	27 (di-:5)
9[b]	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	MeCN (0.4)	20
10[b]	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	MeCN (0.9)	11
11	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	H_2O (0.9)	0
12	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	acetone (0.9)	0
13	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	DMF (0.9)	0
14	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	hexane (0.9)	0
15	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	DCM (0.9)	20
16[b]	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	DCM (0.9)	40 (di-:5)
17[b]	Ag_2CO_3 (40)	Na_2CO_3 (1.5)	0.5	DCM (0.7)	57 (di-:6)
18[b,c]	**Ag_2CO_3 (40)**	**Na_2CO_3 (2.5)**	**0.2**	**DCM (0.7)**	**77 (di-:19)**
19[b,c]	Ag_2CO_3 (40)	Na_2CO_3 (2.5)	0.2	DCM (0.4)	25
20[b,c]	Ag_2CO_3 (20)	Na_2CO_3 (2.5)	0.2	DCM (0.7)	64 (di-:10)
21[b,c]	Ag_2CO_3 (5)	Na_2CO_3 (2.5)	0.2	DCM (0.7)	27
22[b,c]	–	Na_2CO_3 (2.5)	0.2	DCM (0.7)	trace
23	Ag_2CO_3 (10)	Na_2CO_3 (1.5)	0.5	MeCN (0.9)	31
24	–	Na_2CO_3 (1.5)	0.5	MeCN (0.9)	trace

[a]The yields were determined by ^{19}F NMR analysis of crude products using CF_3CH_2OH as the internal standard. [b]The reaction flask was well-sealed. [c]6.1 equiv of TFA.

ditrifluoromethylated products when 0.5 equiv of concd H_2SO_4 was added and CH_3CN (0.9 mL) was used as the solvent. The yield decreased to 11% when the reaction flask was well-sealed. At this point, it remains unclear why a small opening in the reaction flask improves the yield. One possible explanation could be the high sensitivity of the reaction to concentration. For example, reactions with different concentrations provided quite different yields (Table 1, entries 5 and 7, 8 and 9, 18 and 19). When the reaction is performed at elevated temperature, the opening in the reaction flask allows CH_3CN to evaporate, which increases concentration over the course of the reaction.

No trifluoromethylated products were generated when the reactions were carried out in most other solvents. When the reaction was carried out in DCM, however, the desired product was observed in 20% yield. Surprisingly, the reaction yield was enhanced to 40% in a well-sealed flask. The yield was further improved to 57% by increasing the concentration by reducing the volume of DCM to 0.7 mL and by using 6.1 equiv TFA. Lastly, when the quantity of concd H_2SO_4 was decreased to 0.2 equiv, the yield increased to 77%.

Almost no trifluoromethylated products were formed in the absence of Ag_2CO_3 for reactions in either DCM or CH_3CN. Notably, with 20 and 5 mol % Ag_2CO_3 in DCM, the reaction gave the products in 64% and 27% yield, respectively. Likewise, 31% yield was observed with 10 mol % Ag_2CO_3 in CH_3CN. Insights concerning the role of Ag_2CO_3 can be deduced from these data. Use of 40 mol % Ag_2CO_3 led to the highest yield (81%), and at first glance, it appears from this result that the transformation is not catalytic in Ag_2CO_3 because 40 mol % Ag_2CO_3 contains 80 mol % Ag(I). However, the results from the experiments at other Ag_2CO_3 loadings above provide evidence that Ag(I) does in fact turn over under these conditions.

Based on these results, we have established two efficient sets of reaction conditions for the direct trifuoromethylation of terephthalonitrile with TFA: conditions **A** and **B** (Table 2). Next, we investigated the substrate scope with both sets of conditions. Notably, 1 equiv of benzene was transformed into trifluoromethylbenzene in 69% yield. A variety of monosubstituted benzenes containing an electron-withdrawing or -donating group proved to be reactive, giving isomeric mixtures of *o*-, *m*-, and *p*-trifluoromethylated products, as well as small quantities of ditrifluoromethylated products. To further study the functional group compatibility and regioselectivity of the two sets of conditions, we examined the reactivity of a series of *para*-substituted benzonitriles bearing various substituents. As shown in Table 2, the reaction tolerated a range of different functional groups, including Me, F, Cl, Br, I, CF_3, and CO_2Me. It should be mentioned that 3.6 equiv TFA was sufficient to give optimal yields for some of the reactions with conditions **B**. Regioselectivity varied depending on the substrate, but in general, trifluoromethylation occurred preferentially at the positions *ortho* to the cyano group. In addition, trifluoromethylation of *ortho*-substituted benzonitriles was also examined, and both of the *meta*- and *para*-C−H bonds were trifluoromethylated

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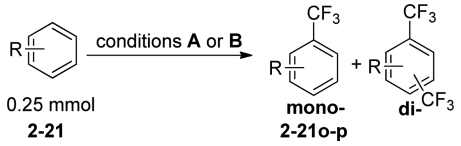
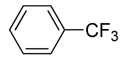
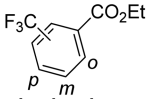
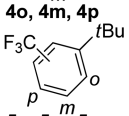
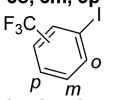
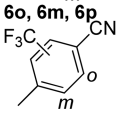
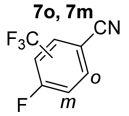
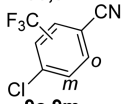
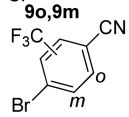
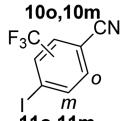
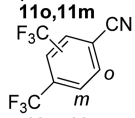
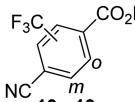
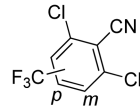
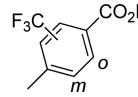
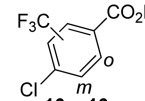
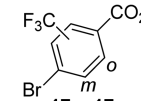
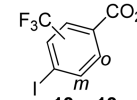
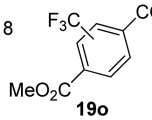
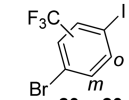
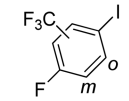
Table 2. Substrate Scope of Trifluoromethylation with TFA



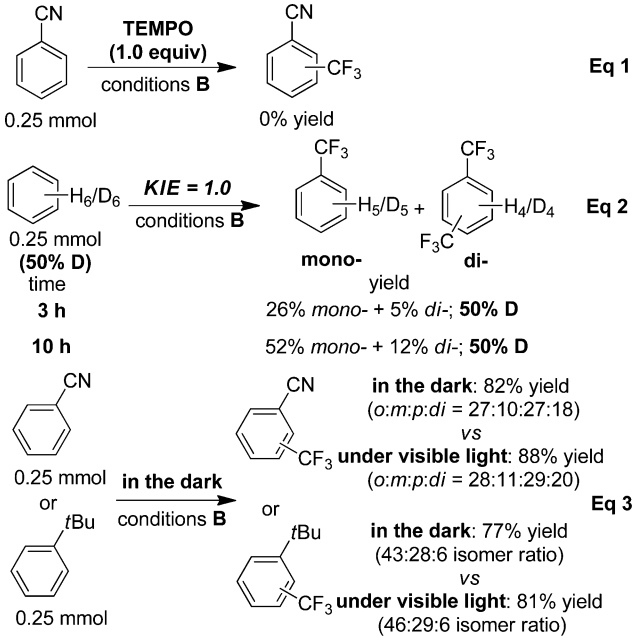
entry	products	yield and [e] isomer ratio
1	 2o	B, 69% (di-:10%)
2	 3o, 3m, 3p	B, 88% (*o:m:p:di* = 28:11:29:20)
3	 4o, 4m, 4p	B, 74% (*o:m:p:di* = 35:11:19:9)
4	 5o, 5m, 5p	B[a], 81% (isomer ratio 46:29:6)
5	 6o, 6m, 6p	A[b, c], 81% (*o:m:p:di* = 25:22:19:15)
6	 7o, 7m	B[a, b], 63% (*o:m:di* = 33:21:9)
7	 8o,8m	B, 73% (*o:m:di* = 42:15:16)
8	 9o,9m	B[a], 48% (*o:m* = 27:21)
9	 10o,10m	B, 78% (*o:m:di* = 36:24:18)
10	 11o,11m	B[a, b], 76% (*o:m:di* = 40:24:12)
11	 12o, 12m	A[b, c], 64% (*o:m:di* = 41:7:16)
12	 13o,13m	B, 57% (*o:m:di* = 21:27:9)
13	 14m,14p	A[b, c], 83% (*m:p:di* = 44:29:10)
14	 15o,15m	B[a], 44% (*o:m* = 26:18)
15	 16o, 16m	B, 60% (*o:m:di* = 29:25:6)
16	 17o, 17m	B, 53% (*o:m* = 29:24)
17	 18o, 18m	B, 76% (*o:m:di* = 35:26:15) B[d], 36%
18	 19o	B, 75% (di-:15%)
19	 20o, 20m	A[b, c], 56% (*o:m:di* = 23:27:6)
20	 21o, 21m	A, 54% (di-:8%) (isomer ratio 20:26)

[a]3.6 equiv of TFA, 1.5 equiv of Na_2CO_3. [b]No concd H_2SO_4. [c]0.4 mL of MeCN. [d]5 mol % of Ag_2CO_3. [e]The yield and isomer ratio were determined by ^{19}F NMR and ^1H NMR using CF_3CH_2OH and CH_2Br_2, respectively, as internal standards. The products were confirmed by GC–MS. Conditions **A**: Ag_2CO_3 (40 mol %), $K_2S_2O_8$ (2.0 equiv), TFA (3.6 equiv), Na_2CO_3 (1.5 equiv), H_2SO_4 (0.5 equiv), MeCN (0.9 mL), 120 °C, 10 h, not well-sealed. Conditions **B**: Ag_2CO_3 (40 mol %), $K_2S_2O_8$ (2.0 equiv), TFA (6.1 equiv), Na_2CO_3 (2.5 equiv), H_2SO_4 (0.2 equiv), DCM (0.7 mL), 120 °C, 10 h.

in a good yield. Likewise, several *para*-substituted methyl benzoates were subjected to conditions **A** and **B**, and the reactions proceeded in acceptable yields to give two isomers. A slight preference for trifluomethylation at the C–H bond *ortho* to the ester group was observed. Finally, substrates bearing two halogen atoms underwent C–H trifluoromethylation in modest yields with conditions **A**.

Next, we carried out a series of mechanistic experiments. The addition of TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (1 equiv) suppressed product formation (Scheme 1, eq 1). This

Scheme 1. Mechanistic Studies of Trifluoromethylation Reaction



result is consistent with a mechanism involving a CF_3· intermediate. When a mixture of benzene and benzene-d_6 in a 1:1 mol ratio was subjected to conditions **B**, the yields of the trifluoromethylated products derived from benzene and benzene-d_6 were almost equal (K_H/K_D = 1.0). This finding suggests that C–H cleavage is not the rate-determining step (Scheme 1, eq 2). Furthermore, for the reactions with rigorous exclusion of light or under visible light, similar yields and regioselectivities of the trifluoromethylated products were obtained (Scheme 1, eq 3), implying that light was not involved in the trifluoromethylation reaction.

On the basis of these experiments and the previous studies,[17–20,22] a radical mechanism for this reaction is proposed (Figure 2). Ag(I) is oxidized by peroxydisulfate to generate Ag(II). The resulting Ag(II) species undergoes electron transfer with trifluoroacetate to yield CF_3CO_2·, which decarboxylates to release CF_3·. Finally, CF_3· reacts with the arene substrate,

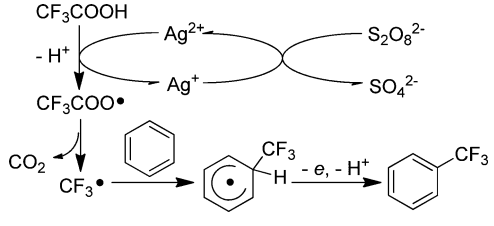


Figure 2. Proposed mechanism for silver-catalyzed C–H trifluoromethylation with TFA.

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affording desired trifluoromethylated product through a radical aromatic substitution reaction.

In summary, we have developed a silver-catalyzed C−H trifluoromethylation reaction of arenes using TFA as the trifluoromethylating reagent. This reaction may open a new avenue for C−H trifluoromethylation with TFA, which has advantages over other CF_3 sources and is in many ways an ideal trifluoromethylation reagent. This reaction provides a new protocol for the generation of CF_3· from TFA, and it has the potential to be extended to other trifluoromethylation reactions with TFA.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures, spectroscopic data of authentic compounds, and characterization of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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