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Letter

Silver-Catalyzed Trifluoromethoxylation of Alkyl Trifluoroborates

Xiaohuan Jiang and Pingping Tang*

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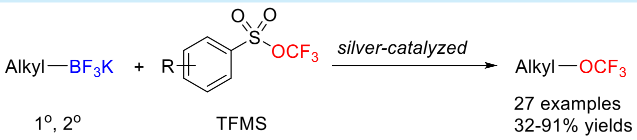
ABSTRACT: A silver-catalyzed trifluoromethoxylation of alkyl trifluoroborates with trifluoromethyl arylsulfonate as the trifluoromethoxylation reagent has been reported for the first time. This reaction is performed under mild reaction conditions and has wide functional group compatibility. In addition, the mechanism of this site-specific trifluoromethoxylation is proposed as a radical pathway.



The metabolic stability and lipophilicity of organic molecules could be increased by introducing "OCF_3" groups, which, in turn, can significantly change their biological properties (Scheme 1a).[1−4] Accordingly, developing new approaches to obtaining trifluoromethoxylated compounds has become a hot topic in synthetic organic chemistry.[5−42] Particularly, radical trifluoromethoxylation is becoming a promising tool to synthesize trifluoromethoxy-containing compounds.[43−46] For example, with the new N-OCF_3 reagents, the radical trifluoromethoxylation of arenes under photocatalytic conditions was reported by Ngai and Togni, respectively.[43−45] Our group has reported the silver-promoted oxidative benzylic C−H trifluoromethoxylation through a radical mechanism.[46] However, site-specific radical trifluoromethoxylation is still challenging.

Scheme 1. Silver-Catalyzed Trifluoromethoxylation of Alkyl Trifluoroborates

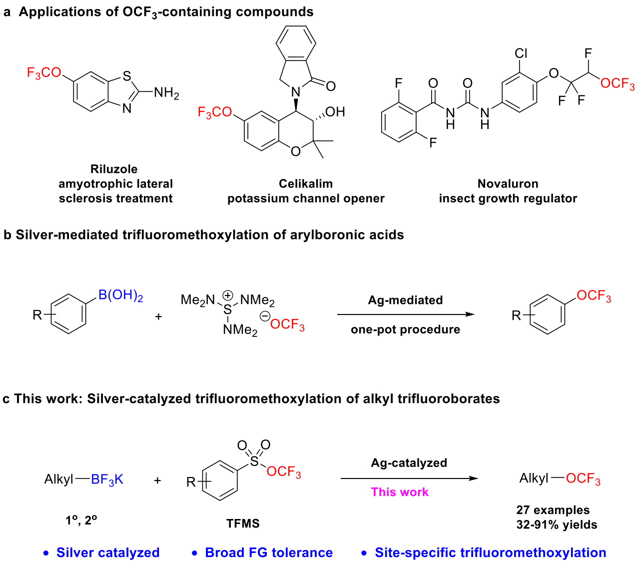
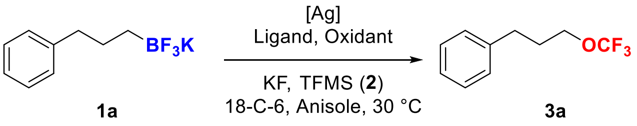


Table 1. Optimization Study[a]



1a

3a

entry	oxidant	silver salt	ligand	yield[b] (%)
1	**Selectfluor**	**AgOTf**	**3,4,7,8-Me_4-Phen**	**91**
2	Selectfluor	AgF	3,4,7,8-Me_4-Phen	88
3	Selectfluor	$AgBF_4$	3,4,7,8-Me_4-Phen	88
4	Selectfluor	no	3,4,7,8-Me_4-Phen	0
5	Selectfluor	AgOTf	Phen	50
6	Selectfluor	AgOTf	4,7-Ph_2-Phen	33
7	Selectfluor	AgOTf	4,7-Me_2-Phen	61
8	Selectfluor	AgOTf	dtbpy	75
9	Selectfluor	AgOTf	no	0
10	$K_2S_2O_8$	AgOTf	3,4,7,8-Me_4-Phen	0
11	PhIO	AgOTf	3,4,7,8-Me_4-Phen	0
12	no	AgOTf	3,4,7,8-Me_4-Phen	0

[a] General conditions: alkyl trifluoroborates (**1a**) (0.05 mmol), oxidants (0.10 mmol), silver salts (30 mmol %), ligands (30 mmol %), KF (0.15 mmol), TFMS (**2a**) (0.15 mmol), 18-C-6 (0.15 mmol), anisole (0.40 mL), N_2 atmosphere, 30 °C. [b] Yields were obtained according to the ^{19}F NMR spectrum, while benzotrifluoride was used as an internal standard.

Organoboron compounds are of great use in many areas, such as medicine, industry and basic science, because of their low toxicity, stability, and easy preparation.[47−49] For example, boronic acid derivatives are valuable cross-coupling partners of the Chan−Lam−Evans reaction[50,51] and the Suzuki−Miyaura

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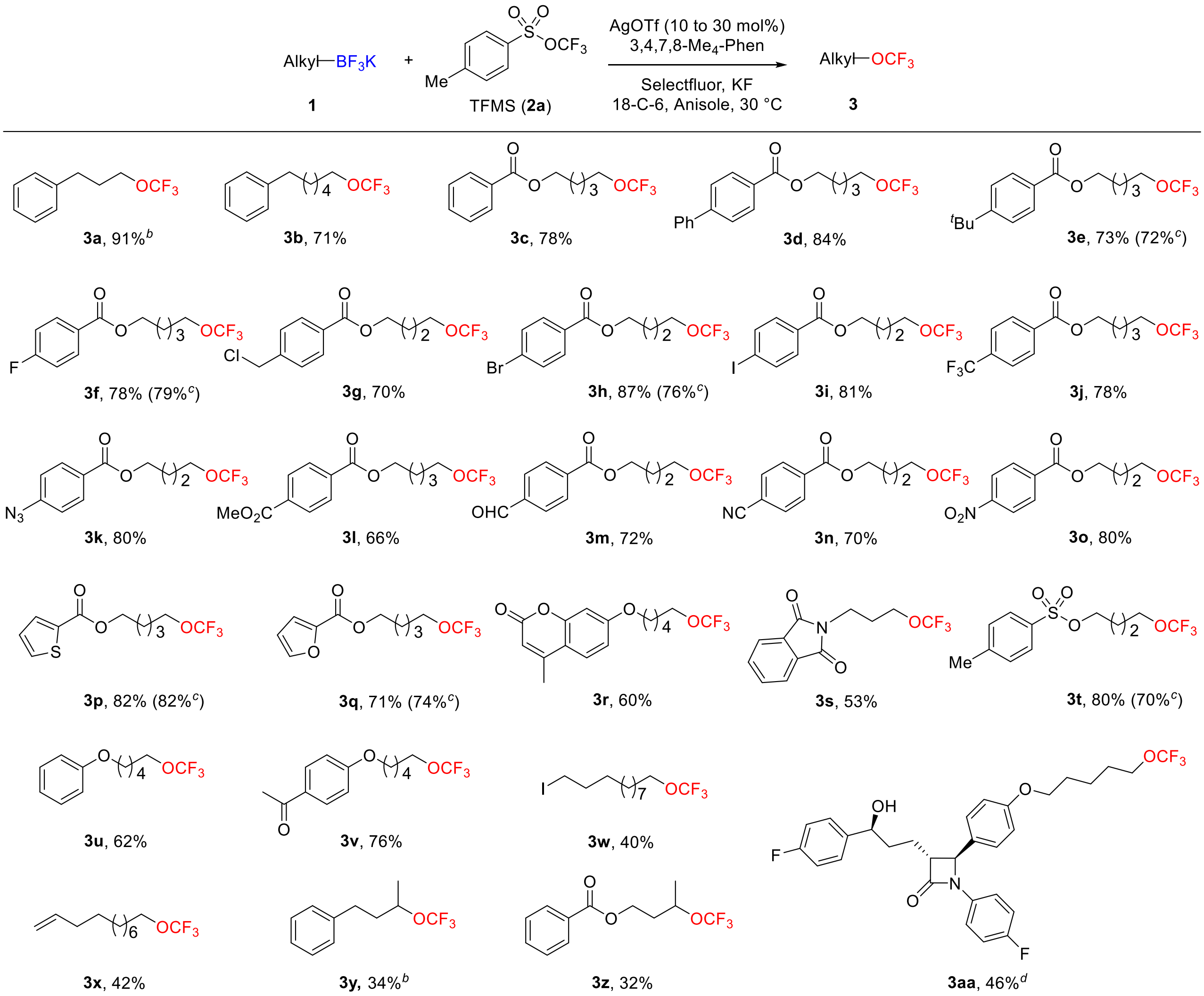
Scheme 2. Scope of the Substrates[a]

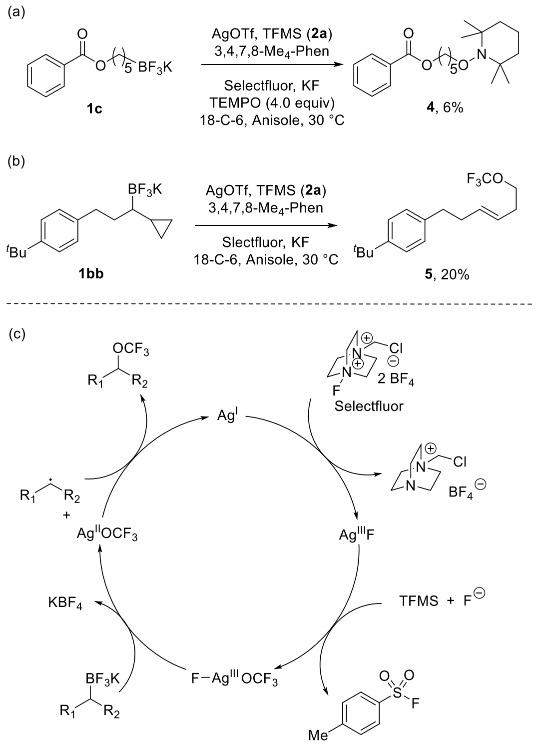


[a]Reaction condition: alkyl trifluoroborates (0.50 mmol), AgOTf (30 mmol %), 3,4,7,8-Me_4-1,10-Phen (30 mmol %), KF (1.50 mmol), TFMS (**2a**) (1.50 mmol), Selectfluor (1.00 mmol), 18-Crown-6 (1.50 mmol), anisole, N_2 atmosphere, 30 °C. [b]Yields were obtained according to the ^{19}F NMR, while benzotrifluoride was used as an internal standard. [c]AgOTf (10 mmol %) and 3,4,7,8-Me_4-1,10-Phen (10 mmol %) were used. [d]KF (2.00 mmol) and TFMS (**2a**) (2.00 mmol) were used.

reaction.[52] In addition, organoborates have been demonstrated to be excellent precursors for alkyl radical species.[53,54] However, transformations about trifluoromethoxylation of organoboron compounds are limited, and only one example was reported. In 2011, Tobias successfully converted aryl stannanes and arylboronic acids into the corresponding aryl trifluoromethyl ethers through a silver-mediated cross-coupling reaction (Scheme 1b).[55] According to what we know, no reaction about the trifluoromethoxylation of alkylboronic acid derivatives has been reported so far. Thus, we developed a first example of trifluoromethoxylation of alkyl trifluoroborates in Ag-catalyzed system with trifluoromethyl arylsulfonate (TFMS, **2**)[56−58] (Scheme 1c).

We recently reported the silver-mediated oxidative trifluoromethoxylation of alkylsilanes through a radical mechanism.[59] We wondered whether the trifluoromethoxylation of alkyl trifluoroborates could also be implemented with a catalytic amount of silver salts. Thus, using potassium (3-phenylpropyl)trifluoroborate **1a** as model substrate and trifluoromethyl arylsulfonate (TFMS, **2**) as trifluoromethoxylation reagent, we performed this reaction in a silver-catalyzed system (see Table 1; more details can be found in the Supporting Information). Different silver salts were screened and AgOTf gave the highest yield (Table 1, entries 1−3). If there were no silver salts, no ideal product **3a** was detected (Table 1, entry 4). The choice of oxidant was important. The use of strong oxidants, such as Selectfluor, was effective, and other oxidants, such as $K_2S_2O_8$, or PhIO, did not give the product (Table 1, entries 10−12). The ligand also has great impact on this reaction (Table 1, entries 5−9). Both phenanthroline and bipyridine could promote this trifluoromethoxylation. Crown ethers were added to this reaction as phase transfer catalysts, which could be used to improve the solubility of KF and alkyl trifluoroborates in anisole. 18-Crown-6 was proven to be the most suitable additive for this transformation, probably because the cavity of 18-Crown-6 and the size of K^+ were well matched. After further optimization of the reaction conditions (Supporting Information), we found the yield can reach up to 91% under the optimal condition of 2.0 equiv Selectfluor, 30 mmol % AgOTf, 30 mmol % 3,4,7,8-

Scheme 3. Mechanistic Experiments and Potential Reaction Pathway



Me_4-1,10-Phen, 3.0 equiv TFMS (**2a**), 3.0 equiv KF, and 3.0 equiv 18-Crown-6 in anisole under N_2 atmosphere at 30 °C. Moreover, if any of these reagents was missing, no desired product would be obtained.

We then investigated the substrate scope for this silver-catalyzed trifluoromethoxylation of alkyl trifluoroborates (Scheme 2). Delightly, a broad scope of alkyl trifluoroborates reacted smoothly and achieved 32% to 91% yields (**3a**−**3z**). Substrates with aryl rings bearing electron-rich and electron-deficient substituents reacted smoothly. Variously important functional groups, such as alkene, hydroxyl, cyano, nitro, amide, ketone, aldehyde, bromo, ether and ester moieties, were well-tolerated, which highlight the compatibility of this method. Notably, substrates with heteroaromatic rings were also successfully processed to give the corresponding products (**3p**, **3q**). What is noteworthy is that the chemoselective trifluoromethoxylation of alkyl trifluoroborates in the presence of alkyl chloride or alkyl *p*-toluenesulfonate was observed. For example, the alkyl trifluoroborate group in substrates **1g**, **1t** was selectively converted to the corresponding "OCF_3" group, while other functional groups, such as alkyl chloride, or OTs remained intact (**3g**, **3t**), which could be used as good leaving groups for further synthetic manipulation. The 40% desired product **3w** was observed, along with 20% ditrifluoromethoxylated byproduct, which is generated by nucleophilic trifluoromethoxylation of alkyl iodide. Moreover, aryl azide was also tolerated (**3k**), and the corresponding product could be further applied in click reaction. Secondary alkyl trifluoroborates were also tested, but lower yields were gained (**3y**, **3z**). The main side product observed was β-H elimination product. Optimization was tried to improve the yield, such as changing ligands, solvents, reaction temperature, and additives, but failed. To our delight, this method could also be applied to the trifluoromethoxylation of a structurally more-complicated molecule, such as ezetimibe derivative (**1aa**, 46% yield). However, only a trace amount of desired product was observed when tertiary alkyl trifluoroborate was applied as a substrate. In addition, gram-scale reaction was performed under the standard condition, and an 80% isolated yield of **3d** was gained. Furthermore, when the equivalents of silver salt and ligand were both reduced to 10 mmol % in this transformation, the yields decreased slightly (**3e**, **3f**, **3h**, **3p**, **3q**, **3t**).

In order to study the mechanism of this transformation, we performed several experiments. In the first, 4.0 equiv of TEMPO was added as the radical trapper, and the TEMPO adduct **4** was observed (Scheme 3a). Furthermore, a radical probe **1bb** was designed and applied in the reaction, and the ring-opening product **5** was achieved in 20% yield (Scheme 3b). These observations indicated that alkyl radicals were generated from alkyl trifluoroborates in this reaction. In addition, no trifluoromethoxylated product was observed when 2−3 equiv of AgF_2 was used instead of AgOTf and Selectfluor, which suggested that a higher valence state of Ag species might be involved in this reaction. Based on the previous reports and above results,[60] a possible mechanism was proposed and described in Scheme 3c. The Ag(I) species is oxidated by Selectfluor to afford Ag(III)-F species,[61−65] then this silver species goes through the ligand exchange to form FAg(III)-OCF_3. The later reacts with alkyl trifluoroborates to give alkyl radicals and Ag(II)OCF_3 via single-electron oxidation. Subsequently, the desired product was obtained by grabbing OCF_3 radical from Ag(II)OCF_3,[60,61,66−68] and Ag(I) was regenerated at the same time. Further invetigations about mechanism are needed to better understand the above reaction.

In conclusion, we have reported, for the first time, about the silver-catalyzed trifluoromethoxylation of alkyl trifluoroborates with TFMS as the trifluoromethoxylation reagent. The highlight of this method is its good tolerance for various functional groups, compared with previous methods. Furthermore, complex small molecules can also be successfully converted to the corresponding trifluoromethoxylated compounds in the late stage. In addition, preliminary mechanistic research was investigated and suggested that the transformation might undergo a free radical pathway. Our next challenge is to achieve asymmetric trifluoromethoxylation of sp^3-hybridized carbon centers.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01741.

Experimental procedures and characterization of all new compounds including ^1H, ^{13}C, and ^{19}F NMR spectra (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Pingping Tang − *State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China;* orcid.org/0000-0002-8296-5695; Email: ptang@nankai.edu.cn

Author

Xiaohuan Jiang − *State Key Laboratory and Institute of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.orglett.0c01741

Notes

The authors declare no competing financial interest.

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