Silver-Mediated Radical Trifluoromethylarylation of Activated Alkenes for the Synthesis of Oxindoles Bearing a CF_3 Group

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Abstract: A radical trifluoromethylarylation of *N*-arylacrylamides with in situ generated [$AgCF_3$] species from Me_3SiCF_3 and AgF in DMF is established through a tandem radical addition and C–H activation pathway. It provided a concise method to prepare 21 examples of CF_3-containing oxindoles within four hours.

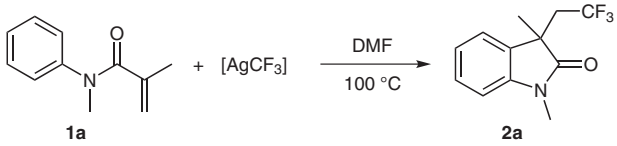
Key words: alkenes, xindole, radical reactions, silver, tandem reaction, trifluoromethylation

Trifluoromethylated molecules are of great interest in pharmaceutical, agrochemistry, and materials science, because of the unique metabolic stability, lipophilicity of the CF_3 group.[1] Great efforts have been made to develop reactions for their syntheses.[2] In 2011, groups of Buchwald, Wang, and Liu have independently reported the copper-catalyzed allylic trifluoromethylation of simple alkenes.[3] Then, the incorporation of a trifluoromethyl group into alkenes, such as oxytrifluoromethylation,[4] hydrotrifluoromethylation,[5] carbotrifluoromethylation,[6] and even aminotrifluoromethylation,[4j,7] has emerged as a powerful tool for C(sp^2/sp^3)–CF_3 bond formation.[8] Among a variety of trifluoromethylation methods, Sanford and Bräse documented the pioneering work for the silver-mediated radical trifluoromethylation of arenes.[9] Nevertheless, the silver-mediated or silver-catalyzed trifluoromethylation reaction is less well explored.[5a,10]

On the other hand, the 3,3-disubstituted oxindole skeleton is present in many natural products, pharmaceuticals, and agrochemicals.[11] The synthetic methods and transformations toward it are currently hot topics.[11,12] In early 2013, Yang and Li independently described a notable access to oxindoles by 1,2-difunctionalization of activated alkenes initiated by corresponding radical species.[13] From then on, the radical-mediated additions and cyclization of *N*-arylacrylamides have received great attention and were applied to synthesize some other oxindole derivatives.[14] In the past years, the synthesis of 3-CF_3 oxindoles has been developed with great progress, while these methods are either imprecise or an expensive trifluoromethyl reagent is necessary. Very recently, Liu[6o] and Fu[6p] demonstrated the trifluoromethylation of *N*-arylacrylamide with Me_3SiCF_3 and $PhI(OAc)_2$, while the reaction time is up to 18 hours. Herein, we report a radical tandem process to afford 3-trifluoroethyl-3′-methyl oxindoles with Me_3SiCF_3 and AgF with shorter reaction time within four hours.

The initial investigation focused on the reaction of *N*-arylacrylamide **1a** with [$AgCF_3$] generated from AgF and Me_3SiCF_3 in DMF because of the good solubility of [$AgCF_3$] in it. To our delight, the desired product **2a** was obtained in 42% yield at the first attempt (Table 1, entry 1). Considering that the [$AgCF_3$] species may decompose more quickly than the rate of the effective conversion the prepared [$AgCF_3$] was added into the reaction mixture through a syringe pump. However, the yield could not be improved (Table 1, entry 2). Next, different concentrations of the substrate **1a** were investigated (Table 1, entries 3–5). In concentrated reaction solution (0.15 M), almost full conversion of **1a** was observed, furnishing **2a** in 74% yield (Table 1, entry 4). No further increase in yield was observed at 0.3 M of **1a** (Table 1, entry 5). Therefore, the optimal concentration of **1a** was 0.15 M.

Table 1 Initial Investigation of the Trifluoromethylation of Arylacrylamide[a]



1a **2a**

Entry	Solvent	Conc. (M)[b]	Yield (%)[c]
1	DMF	0.05	42
2[d]	DMF	0.05	38
3	DMF	0.075	47
4	DMF	0.15	74
5	DMF	0.3	68

[a] *Reaction conditions:* **1a** (0.15 mmol), AgF (3.0 equiv), Me_3SiCF_3 (3.0 equiv), and DMF (volume according to indicated concentration) at 100 °C under argon atmosphere for 4 h.
[b] Concentration of **1a**.
[c] Isolated yield.
[d] The prepared [$AgCF_3$] solution in DMF (2 mL) was added though a syringe pump over a period of 1 h.

For optimization of the reaction conditions, solvents, and temperature were screened at the optimal concentration. However, use of some other solvents failed to promote the desired transformation, such as MeCN, toluene, THF,

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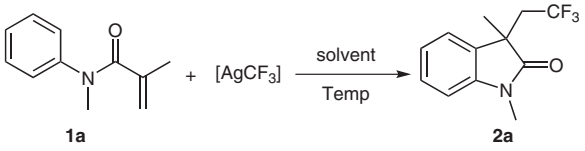
DMSO, and DCE (Table 2, entries 2–5). The reaction temperature showed little influence on the yield (Table 2, entries 6 and 7). Reducing the amount of AgF and Me_3SiCF_3 step by step, a sharp decrease was observed in the conversion of **1a** into **2a** (Table 2, entries 8 and 9). Therefore, the optimal reaction conditions are as follows: DMF as solvent, the substrate concentration 0.15 M, reaction temperature 100 °C, the amount of [$AgCF_3$] 3.0 equivalents.

Table 2 Further Optimization of the Reaction Conditions[a]

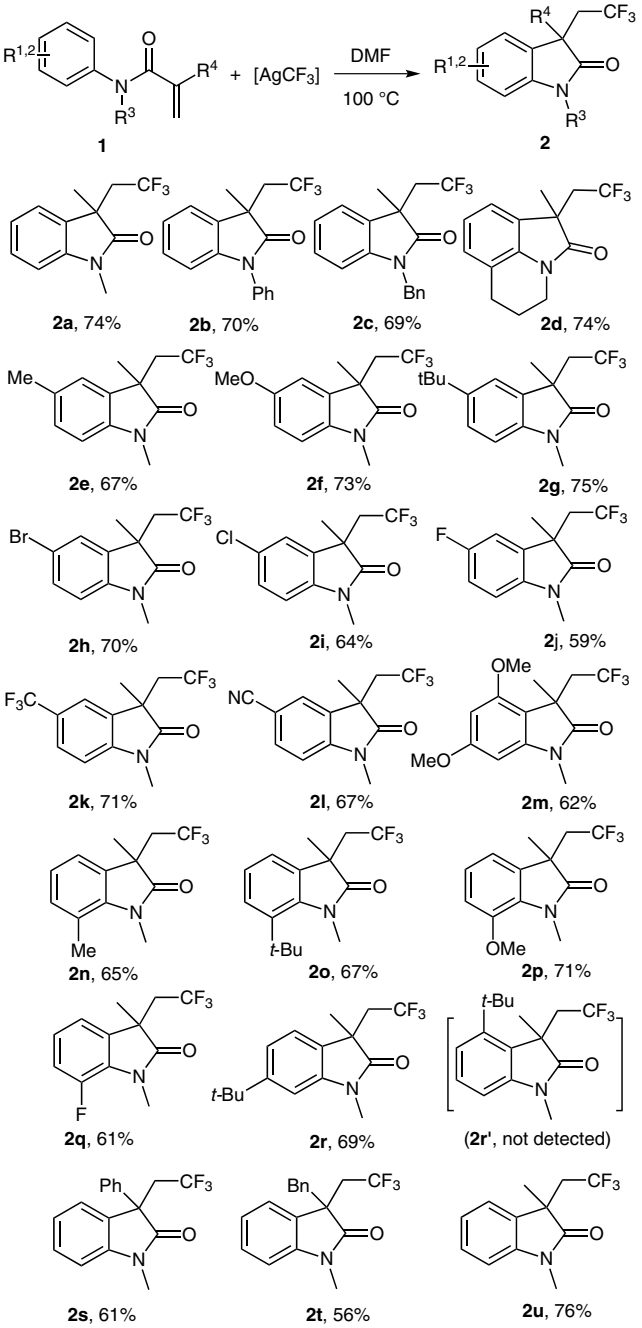


1a **2a**

Entry	Solvent	Temp (°C)	Yield (%)[b]
1	DMF	100	74
2	MeCN	100	69
3	toluene	100	22
4	DMSO	100	22
5	DCE	100	trace
6	DMF	80	55
7	DMF	120	74
8[c]	DMF	100	53
9[d]	DMF	100	24

[a] *Reaction conditions:* **1a** (0.15 mmol), AgF (3.0 equiv), Me_3SiCF_3 (3.0 equiv), and solvent (1 mL, 0.15 M) at 100 °C under argon atmosphere for 4 h.
[b] Isolated yield.
[c] AgF (2.0 equiv), Me_3SiCF_3 (2.0 equiv).
[d] AgF (1.0 equiv), Me_3SiCF_3 (1.0 equiv).

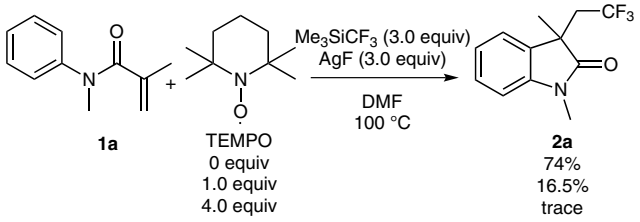
With the optimized conditions, the scope of this radical aryltrifluoromethylation of the *N*-arylacrylamides was investigated as shown in Scheme 1. N-Protected substrates **1a**–**c** bearing methyl, aryl, benzyl, as well as the tetrahydroquinoline derivative **1d** were found to be good for this transformation (69–74% yields). Different *N*-arylacrylamides of substituted aniline were subsequently examined. Both electron-donating and electron-withdrawing groups on the *para* position of the aryl ring afforded products **2e**–**l** in yields of 64–75%. And a similar trend was also noticed with *ortho*-substituted *N*-arylacrylamides **2n**–**q**. In addition, the 3,5-disubstituted derivative provided the corresponding oxindole **2m** in 62% yield. Moreover, the substrate bearing a *tert*-butyl group at the *meta* position exhibited good reactivity in 69% yield and excellent regioselectivity for **2r**. Its regioisomer **2r′** with more steric hindrance was not detected as determined by the ^1H NMR spectroscopy of the crude mixture. It is worth to note that the regioselectivity in similar transformation with 3-methyl, 3-ethyl, or 3-fluoro substituent in the literature is much lower.[6a,d,13,14] Moreover, substrates with different substituents on olefin were examined. α-Substituted olefins bearing aryl and benzyl were tolerant, and converted into products **2s**–**t** smoothly in moderate yields. Finally, heterocyclic substrate **1u** was also tolerated and gave the desired product in 76% yield. In general, all reactions occurred to full conversion within four hours, which is much shorter than the reported procedures.[6a,i,o,p] However, this protocol has its limitations. No reaction occurred in the case of nitrogen-free substrate **1v**, nonterminal alkene such as β-methyl acrylamide (**1w**), and ester or thioester



Scheme 1 Scope of substrate. *Reagents and conditions*: **1** (0.15 mmol), AgF (3.0 equiv), Me_3SiCF_3 (3.0 equiv), and DMF (1 mL, 0.15 M) at 100 °C under argon atmosphere for 4 h. Yields are given for isolated products after column chromatography purification.

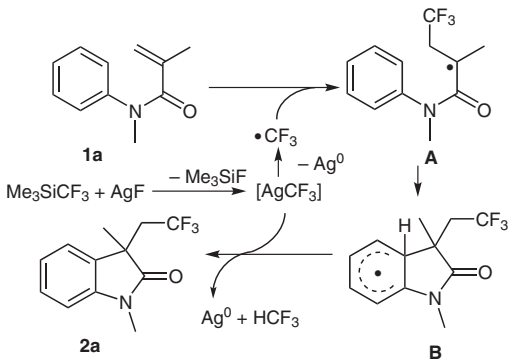
such as phenyl methacrylates **1x** and **1y** (see Supporting Information).

To elucidate the mechanism, 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), a well-known radical trap,[2q,7b] was added in the reaction system. Therefore, the desired product was obtained in only 16.5% yield in the presence of 1.0 equivalent of TEMPO, while the reaction was totally suppressed by 4.0 equivalents of TEMPO (Scheme 2).



Scheme 2 The control experiments using TEMPO

On the basis of the experimental observation and literatures,[9,13a,14b] a possible reaction mechanism was proposed in Scheme 3. This transformation proceeded via a pathway involving the generation of a trifluoromethyl radical ($^{\bullet}CF_3$) from intermediate [$AgCF_3$] species. Initially, the active [$AgCF_3$] species was generated in situ from Me_3SiCF_3 and AgF releasing Me_3SiF in DMF at room temperature. Then, [$AgCF_3$] undergoes single-electron transfer affording the trifluoromethyl radical when it is heated at 100 °C followed by a radical addition to the C=C of **1a** to give radical intermediate **A**, which undergoes an intramolecular addition to the aromatic ring giving radical intermediate **B**. Finally, rearomatization of **B** through a single-electron transfer (SET) process furnishing the product 3-trifluoroethyloxindole (**2a**).



Scheme 3 Proposed mechanism for the trifluoromethylarylation of alkenes with [$AgCF_3$]

In summary, we have developed a silver-mediated trifluoromethylarylation of active alkenes in a tandem way involving a radical C–H activation. This method provides a very concise access to CF_3-containing oxindoles in a short time. The excellent regioselectivity was demonstrated when a *meta*-substituted *N*-arylacrylamide was used. Studies on the synthesis of trifluoromethylated molecules involving trifluoromethyl radical are in progress.

To a Schlenk tube substrate **1** (0.15 mmol), AgF (3.0 equiv), Me_3SiCF_3 (3.0 equiv) and DMF (1 mL) were added under argon. The reaction mixture was stirred at r.t. for 30 min and at 100 °C for another 4 h. After the reaction was finished, the mixture was filtered through a layer of Celite. The filtrate was diluted with EtOAc (100 mL) and washed with H_2O (6 × 1 mL) to remove DMF. The organic layer was dried over anhydrous Na_2SO_4, and solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography (PE–EtOAc = 15:1, v/v) to give the pure product **2**.

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Supporting Information for this article is available online at http://www.thieme-connect.com/products/ejournals/journal/10.1055/s-00000083.

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