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## Graphical Abstract

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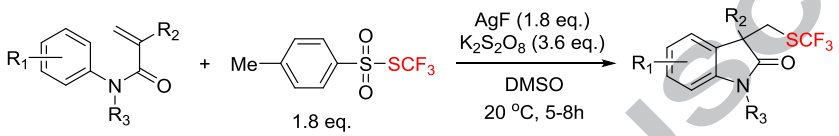

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# Silver-Mediated Radical Aryltrifluoromethylthiolation of Activated Alkenes by *S*-Trifluoromethyl 4-Methylbenzenesulfonothioate

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ABSTRACT

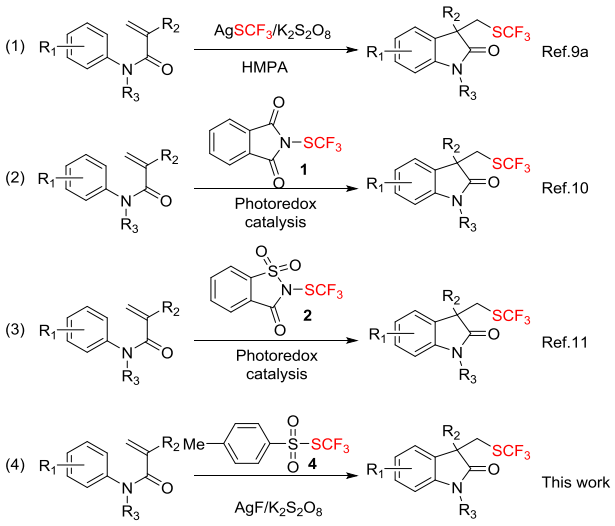
Herein, we describe the preparation of trifluoromethylthiol-substituted oxindoles by silver-mediated aryltrifluoromethylthiolation of activated alkenes, using *S*-trifluoromethyl 4-methylbenzenesulfonothioate as a $F_3CS$ radical source and showing that the reagent availability, mild conditions, and broad functional group compatibility of this transformation make it a viable alternative strategy of constructing $C_{sp3}$–$SCF_3$ bonds.



## 1. Introduction

Trifluoromethylthiolation has recently emerged as a hot organic/medicinal chemistry research field.[1] Since the trifluoromethylthiol ($CF_3S$) group is highly lipophilic (Hansch parameter $\pi_R$ = 1.44)[2] and electron-withdrawing, its incorporation into bioactive molecules can improve their cell membrane permeation ability[3] and metabolic stability,[4] which makes the development of mild and efficient trifluoromethylthiolation methods a task of high significance.

In addition to nucleophilic trifluoromethylthiolation employing $AgSCF_3$,[5] $CuSCF_3$,[6] or $Me_4NSCF_3$[7] as $SCF_3^-$ sources, great progress has been made in the field of electrophilic trifluoromethylthiolation, with a series of easy-to-handle and shelf-stable trifluoromethylthiolation reagents currently being available.[8] However, although a number of aromatic molecules have been trifluoromethylthiolated by the above nucleophilic/electrophilic reagents, the radical trifluoromethylthiolation of alkenes remains underexplored, mainly due to the limited number of reliable methods of generating the $F_3CS$ radical. The most common $F_3CS$ radical source, used in many impressive transformations, is $AgSCF_3$, which, however, is expensive and requires *in situ* oxidation by a strong oxidant to generate the $SCF_3$ radical (Scheme 1, Eq. 1).[9] In 2016, Hopkinson *et al.* reported visible-light-promoted radical trifluoromethylthiolation of styrenes by 2-((trifluoromethyl)thio)isoindoline-1,3-dione (**1**) (Scheme 1, Eq. 2).[10] Recently, Dagousset and Magnier reported visible-light-driven radical trifluoromethylthiolation of alkenes by N-trifluoromethylthiosaccharin (**2**) (Shen's reagent) (Scheme 1, Eq. 3).[11] However, the preparation of compounds **1** and **2** requires the use of expensive $AgSCF_3$ or $CuSCF_3$. In 2016, Shen *et al.* reported an elegant radical-mediated phenylsulfonyl-difluoromethylthio-1,2-difunctionalisation of alkenes by *S*-difluoromethyl benzenesulfonothioate (**3**).[12] Recently, Xu *et al.* reported a gold and visible-light mediated




**Scheme 1** Radical aryltrifluoromethylthiolation of activated alkenes.

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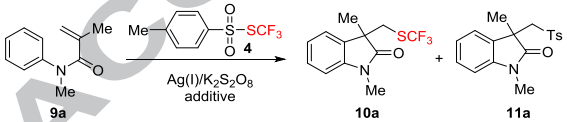
phenylsulfonyl-trifluoromethylthio-1,2-difunctionalisation of alkenes by *S*-trifluoromethyl 4-methylbenzenesulfonothioate (**4**).[13] Due to being interested in the development of efficient C–S bond construction methods,[14] we herein utilised compound **4**, easily prepared from trimethyl(trifluoromethyl)silane (**5**), *N*,*N*-diethyl-1,1,1-trifluoro-l4-sulfanamine (**6**), aniline (**7**), and sodium 4-methylbenzenesulfinate (**8**) in two steps,[8a, 15] as an alternative $F_3CS$ radical source, successfully achieving silver-mediated oxidative aryltrifluoromethylthiolation of activated alkenes to produce trifluoromethylthiol-substituted oxindoles (Scheme 1, Eq. 4).

## 2. Results and discussion

Treatment of *N*-methyl-*N*-phenylmethacrylamide (**9a**) with **4** in the presence of $AgNO_3$, $K_2S_2O_8$, and hexamethylphosphoramide (HMPA) in dimethyl sulfoxide (DMSO) at 40 °C afforded the desired aryltrifluoromethylthiolation product **10a** (24% yield, Table 1, entry 1) and the non-desired arylsulfoxidation product **11a** (40% yield). When the reaction was carried out without HMPA, the yield of **10a** increased to 38%, with only trace amount of **11a** detected (Table 1, entry 2). To optimise the reaction conditions, various oxidants ($Na_2S_2O_8$, $(NH_4)_2S_2O_8$, *t*-BuOOH, and $(t\text{-BuO})_2$ (Table 1, entries 3–6)) were investigated, but none of them was superior to $K_2S_2O_8$, with subsequent screening of silver salts ($AgSbF_6$, AgOTf, and AgF) showing that AgF afforded the best yield (Table 1, entries 7–9). Finally, the loading of **4** and AgF, reaction temperature, reactant concentration, and solvent were examined. When the loadings of **4** and AgF were increased from 1.2 to 1.8 equivalents, the yield of **10a** increased from 42 to 58% (Table 1, entries 10 and 11). However, a further loading increase to 2.0 equivalents was counterproductive (Table 1, entry 12). Decreasing the reaction temperature to 20 °C improved the yield to 71% (Table 1, entry 13), whereas increasing the concentration of **9a** from 0.083 to 0.125 M or decreasing it from 0.083 to 0.063 M diminished the yield (Table 1, entries 14 and 15). When other solvents such as acetonitrile ($CH_3CN$), toluene, and 1-methylpyrrolidin-2-one (NMP) were used, no desired product was obtained, except for DMF, in which case **10a** was isolated in 34% yield (Table 1, entries 16–19). Thus, the optimised reaction conditions for the aryltrifluoromethylthiolation of **9a** were as follows: **9a** (0.25 mmol), **4** (0.45 mmol), AgF (0.45 mmol), $K_2S_2O_8$ (0.9 mmol), and DMSO (3 mL) at 20 °C.

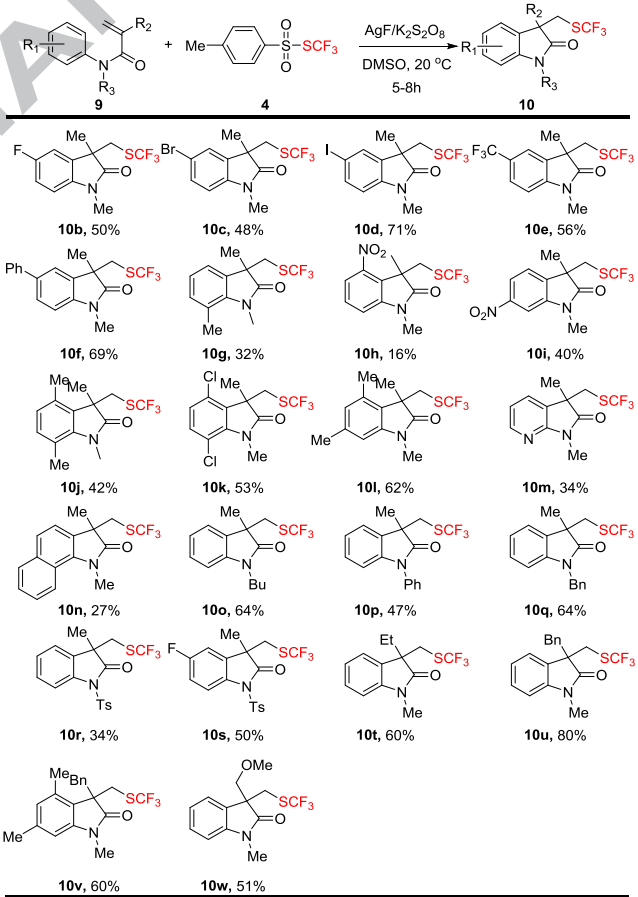
**Table 1.** Optimisation of aryltrifluoromethylthiolation of **9a** by **4** in the presence of diverse silver salts and oxidants.[a]




| Entry | **4**/equiv. | Ag(I)/equiv. | Oxidant/equiv. | Temperature (°C) | Solvent | Yield of **10a** (%)[b] |
|---|---|---|---|---|---|---|
| 1 | 1.2 | $AgNO_3$/1.2 | $K_2S_2O_8$/3.6 | 40 | DMSO | 24[c] |
| 2 | 1.2 | $AgNO_3$/1.2 | $K_2S_2O_8$/3.6 | 40 | DMSO | 38 |
| 3 | 1.2 | $AgNO_3$/1.2 | $Na_2S_2O_8$/3.6 | 40 | DMSO | trace |
| 4 | 1.2 | $AgNO_3$/1.2 | $(NH_4)_2S_2O_8$/3.6 | 40 | DMSO | 29 |
| 5 | 1.2 | $AgNO_3$/1.2 | *t*-BuOOH/3.6 | 40 | DMSO | 0 |
| 6 | 1.2 | $AgNO_3$/1.2 | $(t\text{-BuO})_2$/3.6 | 40 | DMSO | 0 |
| 7 | 1.2 | $AgSbF_6$/1.2 | $K_2S_2O_8$/3.6 | 40 | DMSO | 40 |
| 8 | 1.2 | AgOTf/1.2 | $K_2S_2O_8$/3.6 | 40 | DMSO | 40 |
| 9 | 1.2 | AgF/1.2 | $K_2S_2O_8$/3.6 | 40 | DMSO | 42 |
| 10 | 1.5 | AgF/1.5 | $K_2S_2O_8$/3.6 | 40 | DMSO | 55 |
| 11 | 1.8 | AgF/1.8 | $K_2S_2O_8$/3.6 | 40 | DMSO | 58 |
| 12 | 2.0 | AgF/2.0 | $K_2S_2O_8$/3.6 | 40 | DMSO | 52 |
| 13 | 1.8 | AgF/1.8 | $K_2S_2O_8$/3.6 | 20 | DMSO | 71 |
| 14 | 1.8 | AgF/1.8 | $K_2S_2O_8$/3.6 | 20 | DMSO | 58[d] |
| 15 | 1.8 | AgF/1.8 | $K_2S_2O_8$/3.6 | 20 | DMSO | 65[e] |
| 16 | 1.8 | AgF/1.8 | $K_2S_2O_8$/3.6 | 20 | $CH_3CN$ | 0 |
| 17 | 1.8 | AgF/1.8 | $K_2S_2O_8$/3.6 | 20 | Toluene | 0 |
| 18 | 1.8 | AgF/1.8 | $K_2S_2O_8$/3.6 | 20 | NMP | 0 |
| 19 | 1.8 | AgF/1.8 | $K_2S_2O_8$/3.6 | 20 | DMF | 34 |

[a]Reaction conditions: **9a** (0.25 mmol), **4** (0.3–0.5 mmol), Ag(I) salt (0.3–0.5 mmol), and oxidant (0.9 mmol)) in solvent (3 mL) for 5 h at the indicated temperature. [b]Yield of isolated product after silica gel chromatography. [c]HMPA (0.125 mmol) was used as an additive. [d]DMSO (2 mL) was used. [e]DMSO (4 mL) was used.

With the optimised reaction conditions in hand, the scope of activated alkenes was investigated, with the results presented in Scheme 2. *N*-methyl-*N*-phenylmethacryl amides **9** with both electron-donating and electron-withdrawing substituents in *ortho*-, *meta*-, and *para*-positions of the aniline ring (**9b**–**9l**) were smoothly converted into the corresponding oxindoles. Notably, when *N*-methyl-*N*-(pyridin-2-yl)methacrylamide (**9m**) and *N*-methyl-*N*-(naphthalen-1-yl)methacrylamide (**9n**) were employed as substrates, the desired products **10m** and **10n** were obtained in relatively low yields. Then, other *N*-substitutes-*N*-phenylmethacryl amides (**9o**–**9s**) were tested, affording the desired aryltrifluoromethylthiolation products in moderate yields except for **9r**, which was transformed into **10r** in 34% yield. Finally, α-substituted acrylamides (**9t**–**9w**) were examined, and it was found that ethyl, benzyl, and methoxymethyl substituents were tolerated, and the desired products (**10t**–**10w**) were obtained in moderate to good yields.[16]

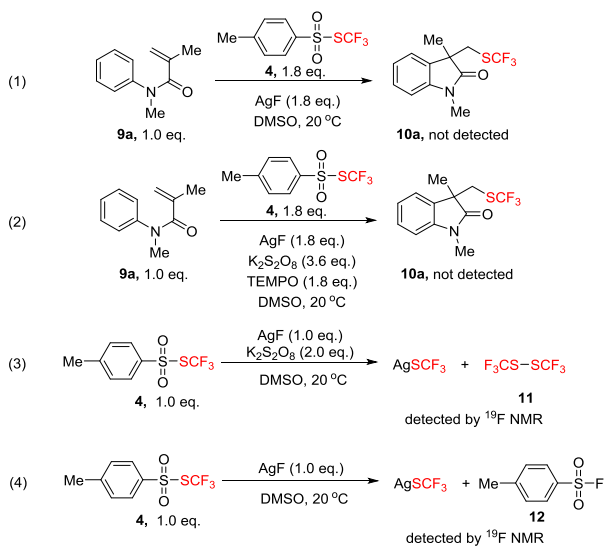



[a] reaction condition: **9b-9w** (0.25 mmol), **4** (0.45 mmol), AgF (0.45 mmol), $K_2S_2O_8$ (0.9 mmol), DMSO (3 mL) at 20 °C

**Scheme 2.** Substrate scope of activated alkene aryltrifluoromethylthiolation.

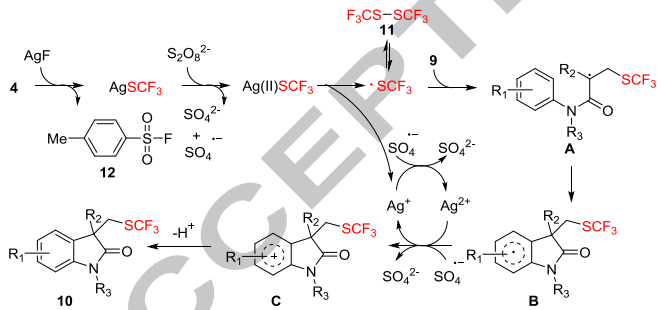
To understand the mechanism of the above transformation, a series of experiments were carried out. In the absence of $K_2S_2O_8$ or in the presence of 1.8 equivalents of TEMPO as a radical scavenger, no desired product was detected (Scheme 3, Eqs. 1 and 2, respectively), which supported the hypothesis that the reaction proceeded via a radical pathway. To gain further insights, **4** was treated with AgF in the presence of $K_2S_2O_8$ in DMSO at 20 °C, and the reaction was monitored by $^{19}$F-NMR for 3 h, with peaks of 1,2-bis(trifluoromethyl)disulfane (**11**) ($\delta$ = –

46.2 ppm) and $AgSCF_3$ ($\delta$ = –20.8 ppm) observed as a result (Scheme 3, Eq. 3).[17] Notably, when **4** was treated with AgF in DMSO at 20 °C for 12 h in the absence of $K_2S_2O_8$, peaks of 4-methylbenzenesulfonyl fluoride **12** (δ = –64.8 ppm) and $AgSCF_3$ were observed (Scheme 3, Eq. 4).[16]




**Scheme 3.** Additional experiments performed to understand the reaction mechanism.

Based on the available literature[9a, 18] and the abovementioned results, the investigated aryltrifluoromethylthiolation was thought to proceed as follows (Scheme 4). Initially, **4** reacts with AgF to form $AgSCF_3$, which is oxidised by $K_2S_2O_8$ to $Ag(II)SCF_3$, with decomposition of the latter species affording Ag (I) and $F_3CS$•. Subsequently, the addition of $F_3CS$• to **9** affords alkyl radical intermediate **A** that cyclises to afford aryl radical **B**. Finally, oxidation of **B** by Ag(II) or $SO_4^{\bullet-}$ followed by deprotonation affords the desired product **10**.




**Scheme 4.** Proposed aryltrifluoromethylthiolation mechanism.

## 3. Conclusion

We have successfully developed silver-mediated radical aryltrifluoromethylthiolation of activated alkenes by 4-methylbenzenesulfonothioate as a $F_3CS$ radical source to afford trifluoromethylthiol-substituted oxindoles. The readily accessible reagents, mild reaction conditions, and broad functional group compatibility of the above transformation make it an alternative and practical strategy of constructing $C_{sp3}$–$SCF_3$ bonds, with the extension of this strategy to other substrates currently being investigated in our lab.

## Acknowledgments

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15. Li, Y.; Qiu, G.; Wang, H.; Sheng, J. *Tetrahedron Lett.* **2017**, *58*, 690-693.
16. General procedure for radical aryltrifluoromethylthiolation of activated alkenes: To a flame-dried Schlenk tube was added activated alkenes **9** (0.25 mmol), AgF (57 mg, 0.45 mmol), $K_2S_2O_8$ (243 mg, 0.9 mmol) and dry DMSO (3 mL). *S*-trifluoromethyl 4-methylbenzenesulfonothioate (**4**) (115

mg, 0.45 mmol) was added to the reaction mixture and the mixture was stirred at 20 °C for 5-8 h. The mixture was diluted with water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic phase was washed with brine, dried over $Na_2SO_4$ and concentrated under reduced pressure to give a residue which was purified by silica gel column chromatography to afford the pure product.
17. See supporting information for detail.
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## Highlights

1. Aryltrifluoromethylthiolation of activated alkenes was achieved.
2. S-trifluoromethyl 4-methylbenzenesulfonothioate was used as $F_3CS$ radical source.
3. Trifluoromethylthiol-substituted oxindoles were prepared.
4. A silver-mediated radical mechanism was proposed.