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Silver-catalyzed cascade radical cyclization of sodium sulfinates and o-(allyloxy)arylaldehydes towards functionalized chroman-4-ones

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ABSTRACT

An efficient method for the synthesis of functionalized Chroman-4-ones via cascade radical cyclization of sodium sulfinates and o-(allyloxy)arylaldehydes using silver as catalyst and $K_2S_2O_8$ as oxidant was presented. The desired products with various groups were isolated in moderate to good yields.

Introduction

The chroman-4-ones are highly valuable structural scaffolds in various natural products, medicinal compounds and biologically active compounds [1–3]. Consequently, significantly efforts have been focused on developing economical, practical and environmentally benign protocols for their preparation [4,5]. As we all know, radical cyclization reaction has been used widely in organic synthesis [6–11]. The radical cyclization reaction using o-(allyloxy) arylaldehydes [12] as substrate represents one of the most efficient way for the synthesis of chroman-4-ones (Fig. 1). For example, Li group synthesize phosphonate chroman-4-ones using silver salt as the catalyst and $K_2S_2O_8$ as an oxidant under mild conditions. This strategy could also extend to azido and hydroxyl radicals, and the synthesis of the corresponding functionalized chroman-4-ones was achieved smoothly [12a]. In 2018, Silver-catalyzed decarboxylative cascade radical cyclization of tertiary carboxylic acids and o-(allyloxy)arylaldehydes was presented by Yu group to synthesize 3-alkyl-substituted chroman-4-one derivatives [13]. Wu and co-workers developed a silver nitrate-catalyzed cascade decarboxylation and oxidative cyclization reaction of a-oxocarboxylic acids and o-(allyloxy)arylaldehydes. With ammonium persulfate as the oxidant, the dihydroflavonoid derivatives can be obtained with moderate to good yields [14a]. Zhu group describe a novel visible light-induced tandem radical addition–cyclization of alkenyl aldehydes with α -bromocarbonyl compounds. The corresponding products are synthesized with high efficiency and good functional group compatibility at room temperature [14b].

As cheap, easily handled strong oxidants, persulfates have been widely used in organic synthesis [15–17]. Persulfates may decompose to sulfate radical anions under heating, light irradiation or transition-metal reductive conditions [18–20]. In 2013, the synthesis of 3-arylthioindoles from indoles and diaryl disulfides using ammonium persulfate in methanol was presented by Kumar and his co-workers [21]. Liu's group found that $(NH_4)_2S_2O8$ was good oxidant for oxidative C—H functionalization of naphthoquinones with alkenes [22]. The direct C—H alkylation of heteroarenes with inactivated ethers promoted by potassium persulfate was developed by Barriault [23]. In view of the above reports, and given our continuing interest in functionalization of heterocyclic compounds [24–29]. Herein, we present Ag/persulfate promoted cyclization of sodium sulfinates and o-(allyloxy)arylaldehydes. Functionalized chroman-4-ones with moderate to high yield can be isolated using this method.

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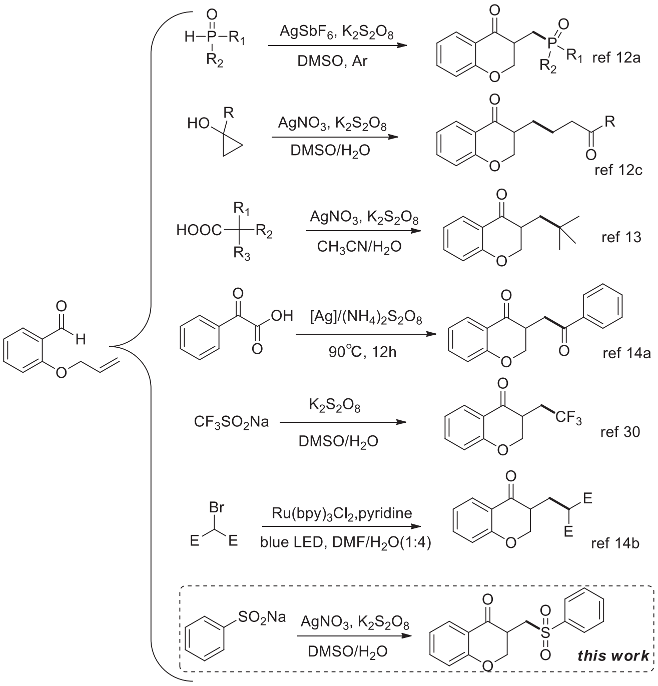


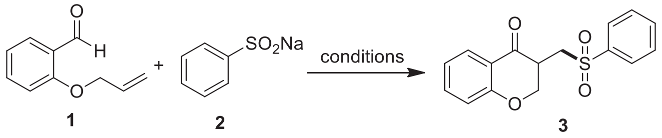
Fig. 1. Synthesis of functionalized chroman-4-ones.

Results and discussion

We initiated our study with examination of the reaction between sodium benzenesulfinate and 2-(allyloxy)benzaldehyde. To our delight, when DMF:H_2O = 1:1 was used as solvent for this reaction, 36% yield of the product was isolated (Table 1, entry 1). Other solvents such as CH_3CN:H_2O (1:1), DCE:H_2O (1:1), PhCl: H_2O (1:1) were also suitable for this transformation (Table 1, entries 2, 3, 7), but the yields were not high. When the reaction was conducted in CH_2Cl_2:H_2O (1:1), toluene:H_2O (1:1) or THF: H_2O (1:1), only trace amount of the products were observed (Table 1, entries 4–6). Dioxane:H_2O (1:1) and DMSO:H_2O (1:1) are proved to be effective for this reaction, providing the desired products in 76% and 78% yields (Table 1, entries 8–9). We next turn our attention to investigate the effect of oxidants on the reaction (Table 1, entries 10–15). $K_2S_2O_8$ was found to be more effective than other oxidant, such as TBHP, DTBP, TBPB, $Na_2S_2O_8$ and $(NH_4)_2S_2O_8$. The sliver catalysts also play an important role in this reaction. Ag_2O, Ag_2SO_4, Ag_2CO_3 and AgOAc could all catalyze the reaction, delivering the desired products in 69–75% yields (Table 1, entries 16–19). No desired product was generated when the reaction proceeded in the absence of sliver catalyst (Table 1, entry 21). This result shows the important role of the sliver catalyst in this transformation. In addition, a slightly lower yield was obtained when the reaction was conducted in air (Table 1, entry 20). Different ratio of DMSO/H_2O were also investigated (Table 1, entry 22–23), showing that DMSO/H_2O (1:1) was the optimal result.

With the optimized reaction conditions in hand, the substrate scope and limitations of the cyclization reaction were investigated by evaluating a variety of sodium sulfinates and o-(allyloxy)arylaldehydes. There was no obvious electronic and steric effect for this reaction (3a–3g, 3m, 3n). For example, CH_3, F, Cl and Br groups are all well tolerated in this system and afford the corresponding products in 62–78% yield. For the substituted o-(allyloxy)arylaldehydes, electron-withdrawing and electron-donating groups did not show obvious influence on the yield (3k–3p). The desired products can be isolated in moderate to high yields. Moreover, halogen atoms (F, Cl, and Br) were well compatible, rendering the product

Table 1
Optimization of the reaction conditions.[a]



Entry	Catalyst (20 mol%)	Oxidant (3 equiv.)	Solvent (2 mL)	Yield (%)
1	$AgNO_3$	$K_2S_2O_8$	DMF:H_2O = 1:1	36
2	$AgNO_3$	$K_2S_2O_8$	CH_3CN:H_2O = 1:1	50
3	$AgNO_3$	$K_2S_2O_8$	DCE:H_2O = 1:1	10
4	$AgNO_3$	$K_2S_2O_8$	CH_2Cl_2:H_2O = 1:1	trace
5	$AgNO_3$	$K_2S_2O_8$	Toluene:H_2O = 1:1	trace
6	$AgNO_3$	$K_2S_2O_8$	THF:H_2O = 1:1	trace
7	$AgNO_3$	$K_2S_2O_8$	PhCl:H_2O = 1:1	12
8	$AgNO_3$	$K_2S_2O_8$	Dioxane:H_2O = 1:1	76
9	$AgNO_3$	$K_2S_2O_8$	DMSO:H_2O = 1:1	78
10	$AgNO_3$	TBHP(in H_2O)	DMSO:H_2O = 1:1	NR
11	$AgNO_3$	TBHP(in decane)	DMSO:H_2O = 1:1	NR
12	$AgNO_3$	DTBP	DMSO:H_2O = 1:1	NR
13	$AgNO_3$	$Na_2S_2O_8$	DMSO:H_2O = 1:1	74
14	$AgNO_3$	$(NH_4)_2S_2O_8$	DMSO:H_2O = 1:1	69
15	$AgNO_3$	TBPB	DMSO:H_2O = 1:1	trace
16	Ag_2O	$K_2S_2O_8$	DMSO:H_2O = 1:1	70
17	Ag_2SO_4	$K_2S_2O_8$	DMSO:H_2O = 1:1	69
18	Ag_2CO_3	$K_2S_2O_8$	DMSO:H_2O = 1:1	75
19	AgOAc	$K_2S_2O_8$	DMSO:H_2O = 1:1	69
20[b]	$AgNO_3$	$K_2S_2O_8$	DMSO:H_2O = 1:1	67
21	–	$K_2S_2O_8$	DMSO:H_2O = 1:1	NR
22	$AgNO_3$	$K_2S_2O_8$	DMSO:H_2O = 1:2	71
23	$AgNO_3$	$K_2S_2O_8$	DMSO:H_2O = 2:1	66

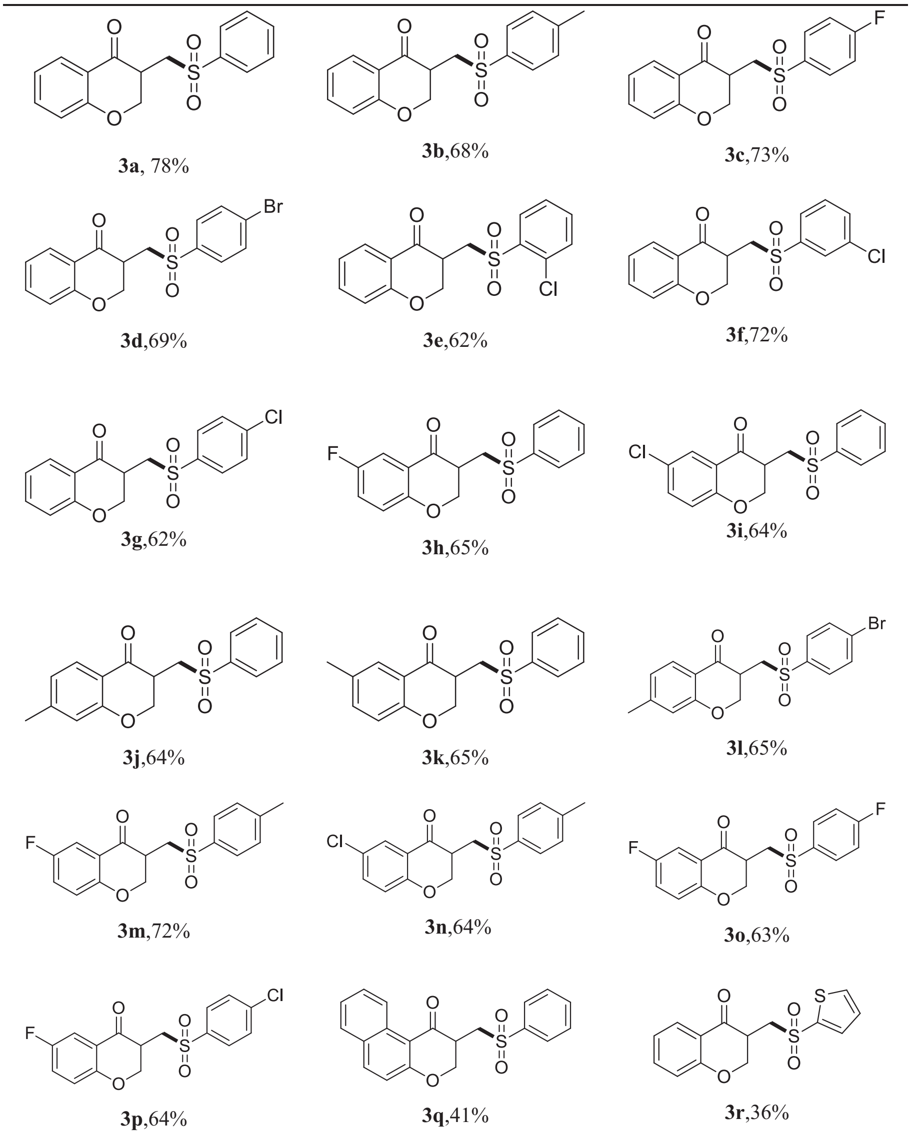
[a] Reaction conditions: **A** (0.2 mmol), **B** (0.4 mmol), catalyst (20 mol%), oxidant (3.0 equiv), solevent (2 mL = 1:1), 100 , N_2, 24 h.

[b] Under air.

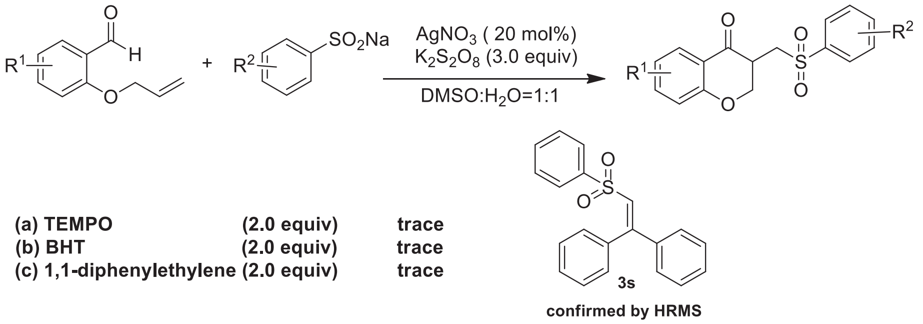
for further functionalizations readily. It should be noted that 2-(allyloxy)-1-naphthaldehyde and 2-hydrosulfonylthiophene are also good substrates for this reaction, albeit the yields of the products was not high (3q, 3r) (Table 2).

In order to further understand the possible mechanism of this novel reaction, a series of control experiments were performed, as shown in Scheme 1. When radical scavenger tempo, BHT or 1,1-diphenylethylene was added to this reaction, the reaction was completely inhibited. Compound **3s** has been confirmed by

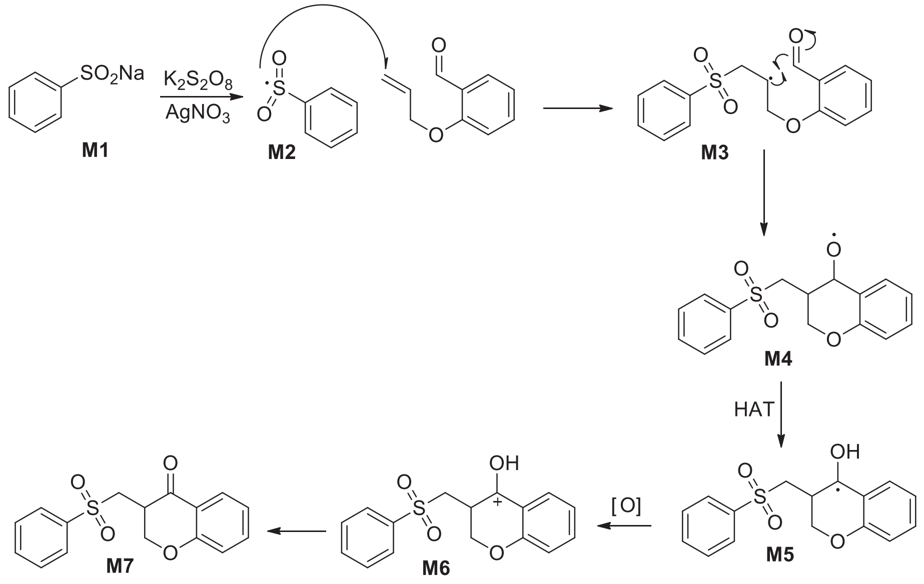
Table 2
Reaction scope.[a]



[a] Reaction conditions: **A** (0.2 mmol), **B** (0.4 mmol), $AgNO_3$ (20 mol%), $K_2S_2O_8$ (3.0 equiv), DMSO:H_2O = 1:1 (2 mL), 100 °C, N_2, 24 h.



Scheme 1. Control experiments.



Scheme 2. Proposed reaction mechanism.

HRMS. This result indicating that a radical process may be proposed for this reaction.

On the basis of the above experimental results and previous reports [30–35], a plausible mechanism was proposed for this reaction (Scheme 2). Firstly, sulfonyl radical **M2** was generated from sodium benzenesulfinate in the presence of $K_2S_2O_8$ and $AgNO_3$. Then reaction between sulfonyl radical **M2** and 2-(allyloxy)benzaldehyde occurred to form **M3**. Subsequently, the **M4** was formed from the intramolecular cyclization reaction of **M3**. Intermediate **M4** suffer from hydrogen atom transfer reaction to produce intermediate **M5**. Finally, the desired product **M7** was formed from the deprotonation of **M6**, which was generated from oxidation of **M5**.

Conclusion

In conclusion, we have developed an efficient method for the synthesis of functionalized chroman-4-ones via cascade radical cyclization of sodium sulfinates and o-(allyloxy)arylaldehydes using silver as catalyst and $K_2S_2O_8$ as oxidant. The desired products with various groups were isolated in moderate to good yields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2020.151704.

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