



Cite this: *RSC Adv.*, 2018, 8, 25961


Received 14th May 2018

Accepted 2nd July 2018

DOI: 10.1039/c8ra04088e

rsc.li/rsc-advances

# Copper(i) reagent-promoted hydroxytrifluoromethylation of enamides: flexible synthesis of substituted-3-hydroxy-2-aryl-3-(2,2,2-trifluoro-1-arylethyl)isoindolin-1-one†

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A novel CuBr-catalyzed hydroxytrifluoromethylation reaction was investigated. Substituted 3-benzylidene-2-arylisindolin-1-ones was reacted with sodium trifluoromethanesulfinate to afford substituted-3-hydroxy-2-aryl-3-(2,2,2-trifluoro-1-arylethyl)isoindolin-1-one. The reaction proceeded at 25 °C in air atmosphere in the absence of base and ligands. Our results indicate that trifluoromethyl free radical tends to attack a double bond rather than aryl in this reaction.

## Introduction

Isoindoles are a series of notable nitrogen-containing compounds known for their bioactivity in nature.<sup>1</sup> In particular, 3-hydroxyisoindolin-1-ones such as **I** and **II** are the core structural motifs of several compounds of medicinal value (Fig. 1). 3-Hydroxy isoindolin-1-ones are known for their use as diuretic and anticancer drugs.<sup>2</sup> As substituted 3-benzylidene-2-arylisindolin-1-ones have double bonds, we try to find a catalytic system for direct hydroxytrifluoromethylation of substituted 3-benzylidene-2-arylisindolin-1-one.

Hydroxytrifluoromethylation of organic molecules has become a research focus in the field of organic synthesis for its unique biological activities.<sup>3</sup> In 1991, Langlois and co-workers reported the first use of CF<sub>3</sub>SO<sub>2</sub>Na as the trifluoromethyl radical source.<sup>4</sup> Since then, a series of trifluoromethylation of olefins by using Langlois reagent has been published in the last

twenty years.<sup>5</sup> In these reactions, CF<sub>3</sub>SO<sub>2</sub>Na was excited by single electron oxidations to generate CF<sub>3</sub> free radicals. The oxidative partners included TBHP,<sup>6</sup> K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>,<sup>7</sup> PhI(OAc)<sub>2</sub>,<sup>8</sup> DTBP,<sup>9</sup> I<sub>2</sub>O<sub>5</sub>,<sup>10</sup> metal (Cu, Mn),<sup>11</sup> photoinducers<sup>12</sup> and so on. There have only been several examples involving hydroxytrifluoromethylation of olefins to afford useful β-trifluoromethyl alcohols.<sup>13</sup> Moreover, there were also studies of the metal-free-catalyzed hydroxytrifluoromethylation reactions of styrenes.<sup>14</sup> Recently, manganese-catalyzed direct hydroxytrifluoromethylation reaction of styrene derivatives has been established.<sup>15</sup> On the other hand, the CuCF<sub>3</sub> system has been used for the synthesis of direct hydroxytrifluoromethylation reaction.<sup>16</sup> Visible light promoted C–F functionalization has been developed under mild reaction condition.<sup>17</sup> Until now, hydroxytrifluoromethylation of enamides has not been reported. As part of our research on the transition metal-catalyzed free radical reaction of substituted 3-benzylidene-2-arylisindolin-1-one,<sup>18</sup> this communication reports the first example of hydroxytrifluoromethylation reaction of 3-benzylidene-2-arylisindolin-1-one (the special structure of enamide) with sodium trifluoromethanesulfinate catalyzed by CuBr in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Scheme 1).

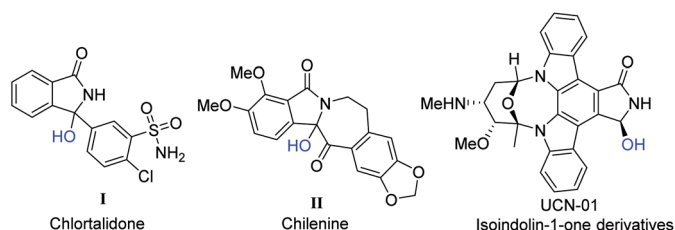


Fig. 1 Bioactive and drug value compounds containing 3-hydroxyisoindolin-1-one motifs.

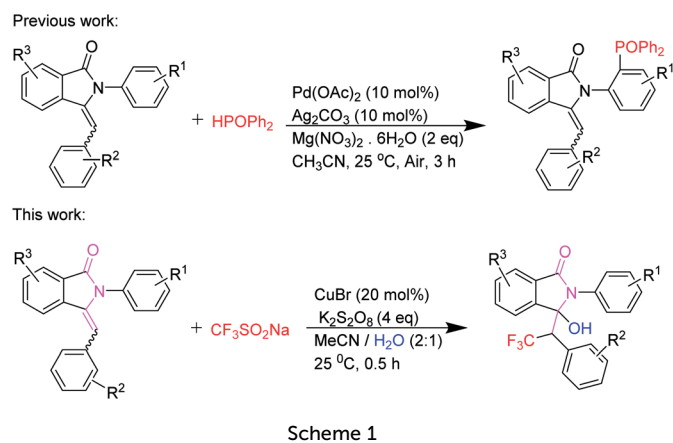
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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c8ra04088e

## Results and discussion

When the model reaction of 3-benzylidene-2-phenylisoindolin-1-one (**1a**) with sodium trifluoromethanesulfinate (**2**) was performed in CH<sub>3</sub>CN/H<sub>2</sub>O in the presence of oxidants such as TBHP, DTBP, Mn(OAc)<sub>3</sub> and PhI(OAc)<sub>2</sub>, no desired products were obtained (Table 1, entries 1, 2, 3 and 4). After the addition of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (4 eq.), the reaction proceeded smoothly to afford the desired product, 3-hydroxy-2-phenyl-3-(2,2,2-trifluoro-1-phenylethyl)isoindolin-1-one (**3a**) in 48% yield (Table 1, entry 5). Further investigation of copper catalysts, the yield of **3a** was





improved to 72% when we used CuBr as the catalyst (Table 1, entries 9). On the other hand, when we use FeCl<sub>3</sub> in place of CuBr, the reaction afforded the desired product in a lower yield (Table 1, entry 12). By screening polar mixed solvents such as DMSO/H<sub>2</sub>O, DMF/H<sub>2</sub>O, THF/H<sub>2</sub>O, acetone/H<sub>2</sub>O, and a representative nonpolar solvent, toluene (Table 1, entries 15–19), we found that CH<sub>3</sub>CN/H<sub>2</sub>O (2 : 1) works best for the reaction. Apart from the above-mentioned factors, the effects of catalyst loading, reaction temperature and time were also investigated, and the optimal reaction conditions were determined to be room temperature reaction for 0.5 h in air atmosphere, with the addition of 20 mol% CuBr as catalyst, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as single electron oxidation reagent and CH<sub>3</sub>CN/H<sub>2</sub>O as solvent (Table 1, entries 20–27).

With the promising results obtained in the model reaction, we subsequently examined the substrate scope of 3-benzylidene-2-arylisindolin-1-one under the optimized reaction conditions (20 mol% CuBr as catalyst, and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as

Table 1 Optimization of the reaction conditions<sup>a</sup>

Entry	Catalyst (%)	Oxidant	Temperature	Solvent (66.7%)	Yield <sup>b</sup>
1		TBHP	25 °C	CH <sub>3</sub> CN	N.D
2		DTBP	25 °C	CH <sub>3</sub> CN	N.D
3		Mn(OAc) <sub>3</sub>	25 °C	CH <sub>3</sub> CN	N.D
4		PhI(OAc) <sub>2</sub>	25 °C	CH <sub>3</sub> CN	N.D
5		K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	48%
6	CuO (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	30%
7	Cu(OAc) <sub>2</sub> (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	55%
8	CuCl (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	60%
9	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	72%
10	CuI (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	28%
11	CuBr <sub>2</sub> (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	50%
12	FeCl <sub>3</sub> (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	45%
13	Ag <sub>2</sub> CO <sub>3</sub> (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	48%
14	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	48%
15	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	DMSO	6%
16	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	DMF	10%
17	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	THF	37%
18	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	Acetone	55%
19	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	Toluene	0%
20	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50 °C	CH <sub>3</sub> CN	65%
21	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	80 °C	CH <sub>3</sub> CN	60%
22	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	10 °C	CH <sub>3</sub> CN	66%
23 <sup>c</sup>	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	35%
23 <sup>d</sup>	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	28%
23 <sup>e</sup>	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	70%
24 <sup>f</sup>	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	46%
25 <sup>g</sup>	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	70%
26 <sup>h</sup>	CuBr (20)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	70%
27	CuBr (10)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	25 °C	CH <sub>3</sub> CN	60%

<sup>a</sup> Reaction conditions: **1a** (1 mmol), **2**, (3 mmol), CuBr, (0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (4 mmol), solvent (10 ml), at 25 °C in air atmosphere, 30 min. <sup>b</sup> Yields are given for isolated products. <sup>c</sup> CH<sub>3</sub>CN/H<sub>2</sub>O = 5/1. <sup>d</sup> CH<sub>3</sub>CN/H<sub>2</sub>O = 1/1. <sup>e</sup> K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (5 mmol) was added. <sup>f</sup> K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (3 mmol) was added. <sup>g</sup> 1 h. <sup>h</sup> In argon atmosphere.



oxidant in CH<sub>3</sub>CN/H<sub>2</sub>O (2 : 1) at 25 °C, for 0.5 h in air atmosphere).

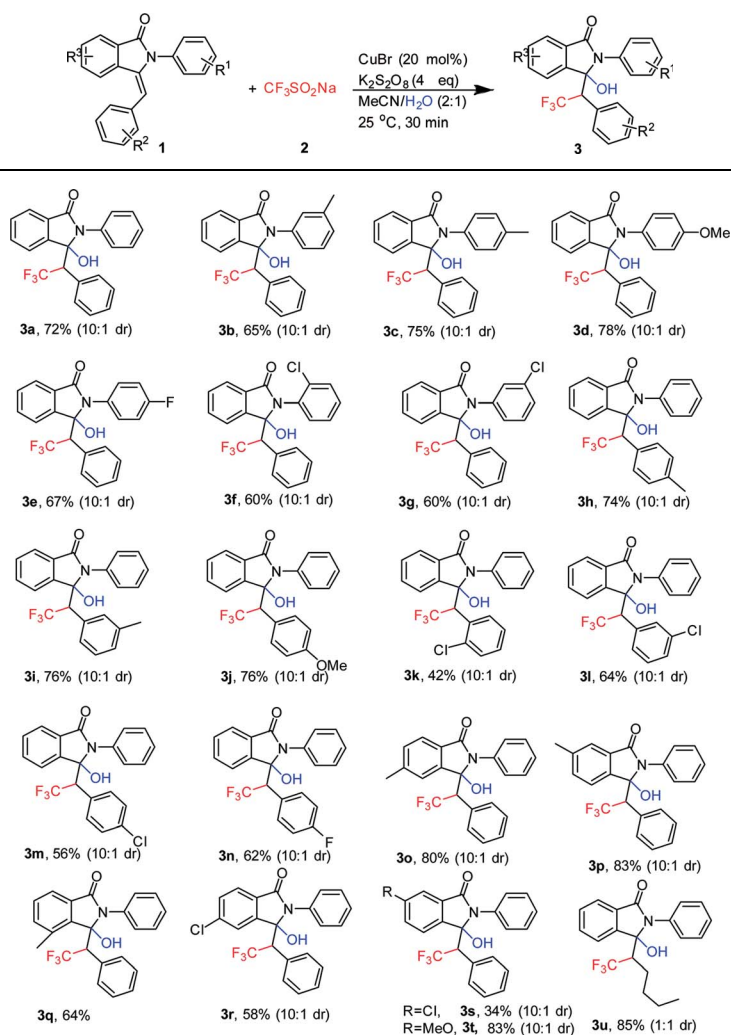
As shown in Table 2, electron-donating substituents such as methyl and methoxy groups on the aryl ring of substituted 3-benzylidene-2-arylisindolin-1-one (**1**) facilitated the reaction to afford the hydroxytrifluoromethylation products (**3**) in moderate to good yields (Table 2, 65–83%, **3a–3d**, **3h–3j**, **3o–3p**, and **3t**). On the contrary, election-withdrawing groups such as F and Cl were unfavorable for the reaction and led to lower yields (Table 2, 34–67%, **3e–3g**, **3k–3n** and **3r–3s**). We also found that when the substrate was 3-pentylidene-2-phenylisindolin-1-one, the target product (**3u**) was in 85% yield but diastereomeric ratio is 1 : 1.

In order to understand the reaction mechanism, following control experiments were carried out. We repeated the reaction in the presence of radical quencher 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and none of **3a** was

obtained (Scheme 2a). The result suggested that free radical were probably generated during the reaction. Furthermore, **3a** was also not detected when the reaction was performed with the addition of butylated hydroxytoluene (BHT, 3.0 equiv.) under the standard conditions (Scheme 2b). Tri-fluoromethylation products was obtained when 1,1-diyldibenzene and Langlois reagent were carried out in standard condition (Scheme 2c). On the other hand, neither aryl amine nor benzylamine substrate produced the *ortho*-position C–H activated products (Scheme 2d).<sup>18</sup> These results indicated that the reaction is only suitable for enamine substrates which have enough electron cloud density.

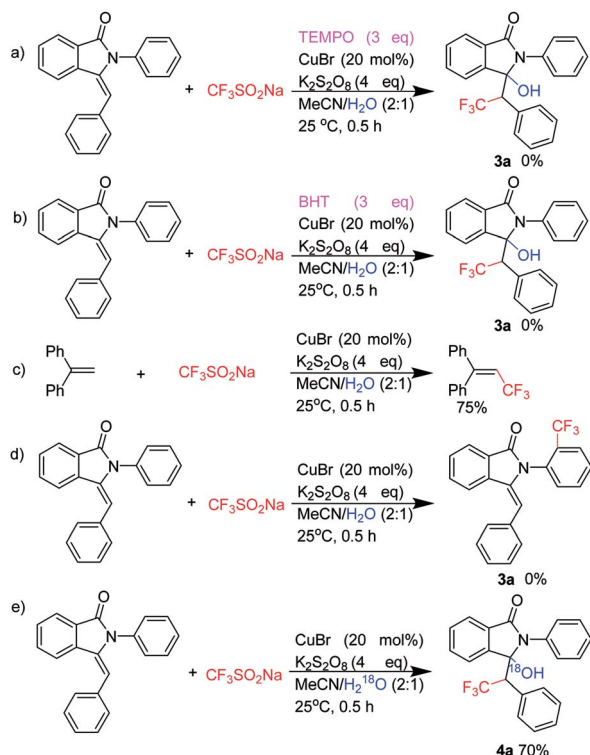
As the hydroxytrifluoromethylation always took place under argon atmosphere in the above experiments, we wondered whether the reaction would proceed if isotopically labelled molecular H<sub>2</sub><sup>18</sup>O was used. Hence, we did further reactions (Scheme 2e). Surprisingly, the corresponding <sup>18</sup>O-containing

Table 2 Scope studies of 3-hydroxy-2-phenyl-3-(2,2,2-trifluoro-1-phenylethyl)isindolin-1-one<sup>a</sup>



<sup>a</sup> Reaction conditions: **1** (1 mmol), **2** (3 mmol), CuBr, (0.2 mmol), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (4 mmol), CH<sub>3</sub>CN/H<sub>2</sub>O 2 : 1 (10 ml), at 25 °C in air atmosphere, 30 min. Yield of isolated products are given.



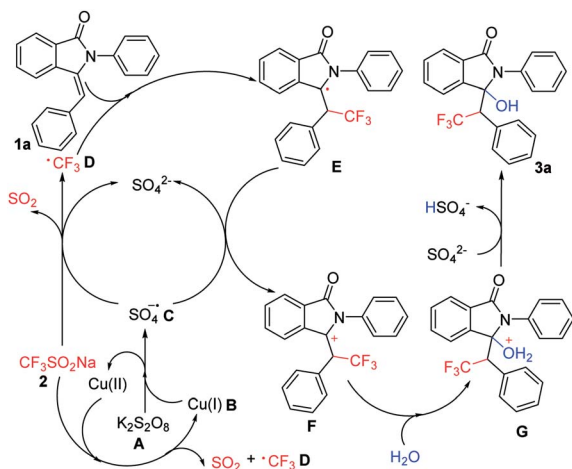


Scheme 2 Control experiments.

product **4a** was obtained in 70%. These results further indicated that the oxygen source of this reaction is derived from  $\text{H}_2\text{O}$  rather than oxygen gas.

On the basis of the mechanistic studies and experimental results, a plausible mechanism is proposed in Scheme 3.

Initially, the  $\text{K}_2\text{S}_2\text{O}_8$  (**A**) was excited by  $\text{Cu}(\text{I})$  (**B**) to generate the intermediate  $\text{SO}_4$  radical anions (**C**), which then reacted with  $\text{CF}_3\text{SO}_2\text{Na}$  (**2**) to form trifluoromethyl free radical (**D**). **D** underwent addition with substrate (**1a**) to form key radical intermediate **E**. Thereafter, the radical intermediate **E** was oxidized by  $\text{SO}_4$  radical anions (**C**) which can regenerate  $\text{SO}_4^{2-}$  to produce the cation intermediate **F**. Due to the presence of  $\text{H}_2\text{O}$ , the cation intermediate **F** underwent nucleophilic



Scheme 3 Proposed reaction mechanism.

addition to generate the corresponding intermediate **G**. The cation intermediate **G** underwent removing protons to generate the corresponding product **3a** and  $\text{HSO}_4^-$ . Finally,  $\text{Cu}(\text{II})$  was reduced to  $\text{Cu}(\text{I})$  by  $\text{CF}_3\text{SO}_2\text{Na}$  (**2**) to complete the catalytic cycle.

## Conclusions

In summary, we have developed a novel catalytic system for direct hydroxytrifluoromethylation of substituted 3-benzylidene-2-arylisindolin-1-ones *via* a radical pathway. The reaction has a high regioselectivity as the  $\text{CF}_3$  free radical is prone to attacking a double bond rather than the aryl. The method has a broad scope and offers a good yield. The corresponding products are potentially useful in drug discovery.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

We gratefully acknowledge financial support from the Prospective Study Program of Jiangsu (BY2015039-08), the Project of Scientific and Technologic Infrastructure of Suzhou (SZS201708), and the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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