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Manganese(III)-mediated direct C_{sp2}–H radical trifluoromethylation of coumarins with sodium trifluoromethanesulfinate†

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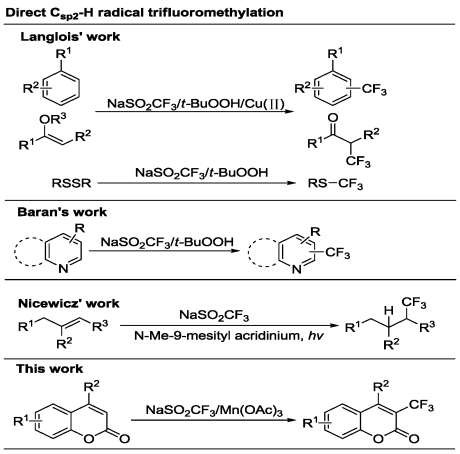
$Mn(OAc)_3$-mediated direct C_{sp2}–H radical trifluoromethylation of coumarins with CF_3SO_2Na (Langlois reagent) to afford selective 3-trifluoromethyl coumarins in moderate to good yields is described. This methodology can also be applied to the trifluoromethylation of quinolinones and pyrimidinones.

Trifluoromethylation has gained increasing interest in recent years as fluorinated compounds possess wide and specific bioactivities and have good solubility and lipophilicity which leads to better membrane permeability and bioavailability than their non-fluorinated analogues, otherwise, they are more stable in the metabolic process because they are more difficult to oxidize.[1] Along with the transition metal-mediated or catalyzed coupling reaction of trifluoromethyl reagents with functionalized substrates,[2,3] radical trifluoromethylation plays an important role in this area.[4]

Sodium trifluoromethanesulfinate (CF_3SO_2Na, Langlois reagent) is one of the CF_3 radical sources, it was first applied in trifluoromethylation of aromatic compounds by Langlois in 1991,[5a] later extended to enol ethers and disulfides (Scheme 1),[5b–d] and recently to biaryls.[5e] Baran reported the trifluoromethylation of nitrogen-containing heteroarenes with the CF_3SO_2Na/*t*-BuOOH system (Scheme 1);[6] Nicewicz described the hydrotrifluoromethylation of alkenes with CF_3SO_2Na using N-Me-9-mesityl acridinium as a photoredox catalyst[7] (Scheme 1). In recent years, Cu-mediated or catalyzed coupling reactions of CF_3SO_2Na with aryl-/vinylboronic acids and unsaturated organotrifluoroborates[4h,8] and copper-/iron-catalyzed decarboxylative trifluoromethylation of α,β-unsaturated carboxylic acids have been reported.[9]



Scheme 1

Coumarins are significant natural products, which display wide and interesting pharmacological properties such as anti-breast cancer,[10] anti-HIV,[11] anti-Alzheimer,[12] vasorelaxant and platelet antiaggregatory activities.[13] In coumarin derivatives, 3-trifluoromethyl coumarins were not easily accessible as 4-trifluoromethyl coumarins.[14] In general, introduction of fluorine atoms into medicinal molecules will increase their bioactivities, so we became interested in exploring direct trifluoromethylation. In our recent studies, we reported the direct phosphonylation of arenes,[15] heteroarenes[16] and alkenes[17] with dialkylphosphites and the diphenylphosphine oxide/$Mn(OAc)_3$ system. Our goal is to develop a novel, selective and efficient method for direct trifluoromethylation of coumarins and other heteroarenes. Herein, we report a general, straightforward method for trifluoromethylation of coumarins with CF_3SO_2Na mediated by $Mn(OAc)_3$ (Scheme 1). Based on the ease of use, safety, environment-friendly nature and cost, we evaluated CF_3I, CF_3SO_2Cl, CF_3SO_2SPh, the Togni reagent, the Langlois reagent and Me_3SiCF_3, which are potent sources of CF_3 radicals, eventually, the Langlois reagent (CF_3SO_2Na, a benchtop stable and inexpensive solid) was selected as the CF_3 radical source. Initially, when CF_3SO_2Na/*t*-BuOOH

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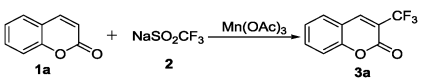
Table 1 Optimization of the reaction conditions[a]

Entry	Oxidant	1a : oxidant	Solvent	Temp (°C)	Yield[b]
1	*t*-BuOOH	1 : 5	$CH_2Cl_2 : H_2O$	25	N.R.[c]
2	*t*-BuOOH	1 : 5	HOAc	25	N.R.
3	*t*-BuOOH–cat	1 : 5	$CH_2Cl_2 : H_2O$	25	N.R.[c,d]
4	CAN	1 : 1	HOAc	25	N.R.
5	$FeCl_3$	1 : 1	HOAc	25	10
6	MnO_2	1 : 1	HOAc	25	12
7	$Mn(OAc)_3$	1 : 1	HOAc	25	26
8	$Mn(OAc)_3$	1 : 3	HOAc	25	50
9	$Mn(OAc)_3$	1 : 3	MeCN	25	16
10	$Mn(OAc)_3$	1 : 3	CH_2Cl_2	25	25
11	$Mn(OAc)_3$	1 : 3	EtOH	25	15
12	$Mn(OAc)_3$	1 : 4	HOAc	25	56
13	$Mn(OAc)_3$	1 : 5	HOAc	25	46
14	$Mn(OAc)_3$	1 : 4	HOAc	50	45
15	$Mn(OAc)_3$	1 : 4	HOAc	60	43
16	$Mn(OAc)_3$	1 : 4	HOAc	80	30

[a] Reaction conditions: coumarin (0.1 mmol) and CF_3SO_2Na (0.3 mmol), 24 h. [b] Isolated yield. [c] The ratio of $CH_2Cl_2 : H_2O$ is 3 : 1, N.R. indicates no reaction. [d] Using 20% mmol $CuSO_4$ as catalyst.

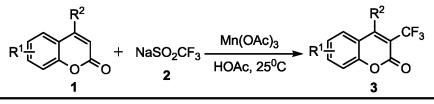
and CF_3SO_2Na/*t*-BuOOH/cat. Cu(II) systems were applied to the trifluoromethylation of coumarin (**1a**), no reaction was observed (Table 1, entries 1–3). Then, the other metal oxidants such as CAN, $FeCl_3$, MnO_2 and $Mn(OAc)_3$ were employed for the reaction, the results indicated that $Mn(OAc)_3$ gave only one trifluoromethylated product in 26% yield (Table 1, entries 4–7), its structure was characterized to be 3-trifluoromethyl coumarin (**3a**) by ^1H, ^{13}C, ^{19}FNMR and HRMS spectral analyses (Scheme 2). It showed that this reaction is regioselective, the trifluoromethylation occurred only at the α-position of the carbonyl group in the pyranone ring, so $Mn(OAc)_3$ was selected as an oxidant for trifluoromethylation. When using 3 equivalents of $Mn(OAc)_3$ for the reaction, the yield reached 50% (Table 1, entry 8). Solvents such as MeCN, CH_2Cl_2, HOAc and EtOH were screened; HOAc gave the best yield (Table 1, entries 8–11). The ratio of **1a : 2 :** $Mn(OAc)_3$ was optimized, and it was found that 1 : 3 : 4 is good for the reaction (Table 1, entries 12 and 13). Raising temperature caused yield reduction, it may be attributed to self-coupling of CF_3 radicals at higher temperatures (Table 1, entries 14–16). Eventually, the optimal reaction conditions were determined to be: a mixture of coumarin (0.1 mmol), CF_3SO_2Na (0.3 mmol) and $Mn(OAc)_3$ (0.4 mmol) in HOAc (3 mL), stirred at 25 °C for 24 h.

Subsequently, different coumarins were used for the reaction and it was found that coumarins bearing electron-donating groups like Me and OMe on the phenyl ring afforded the expected 3-trifluoromethylated coumarins in 50–56% yields (Table 2, entries 1–5). However, when CH_3 groups occupied the 8-position of coumarins, the yield was lowered to 44–45%, this was attributed to the formation of a di-trifluoromethylated by-product (Table 2, entries 6 and 7). In contrast, coumarins bearing electron-withdrawing



Scheme 2

Table 2 Reactions of coumarin **1** and sodium trifluoromethanesulfinate **2**[a]



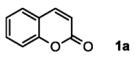
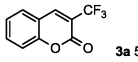
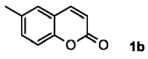
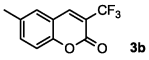
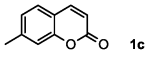
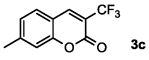
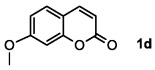
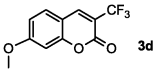
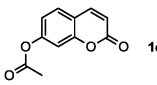
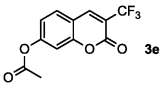
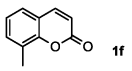
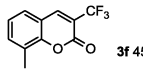
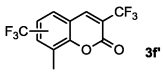
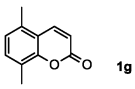
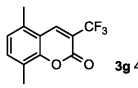
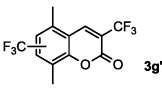
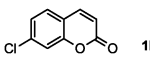
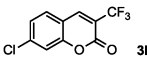
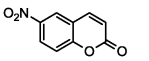
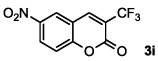
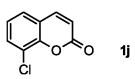
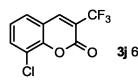
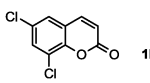
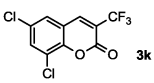
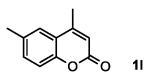
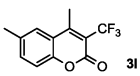
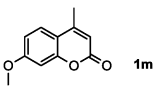
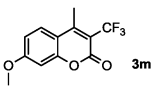
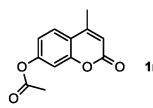
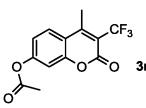
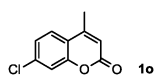
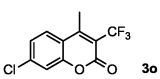
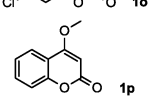
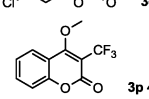
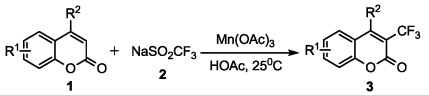
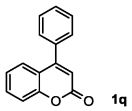
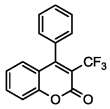
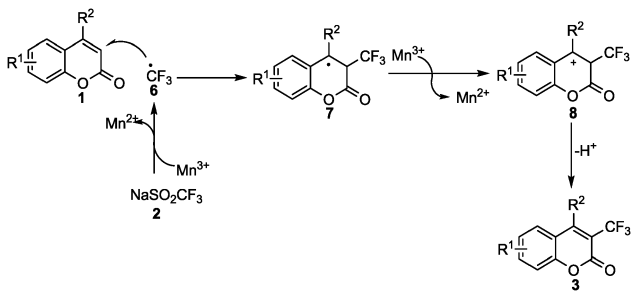
Entry	Coumarin **1**	Products **3** and yield[b]
1	 **1a**	 **3a** 54%
2	 **1b**	 **3b** 50%
3	 **1c**	 **3c** 54%
4	 **1d**	 **3d** 56%
5	 **1e**	 **3e** 54%
6	 **1f**	 **3f** 45%  **3f'** minor[c]
7	 **1g**	 **3g** 44%  **3g'** minor[c]
8	 **1h**	 **3h** 65%
9	 **1i**	 **3i** 63%
10	 **1j**	 **3j** 66%
11	 **1k**	 **3k** 70%
12	 **1l**	 **3l** 55%
13	 **1m**	 **3m** 58%
14	 **1n**	 **3n** 59%
15	 **1o**	 **3o** 68%
16	 **1p**	 **3p** 49%

Table 2 (*continued*)



Entry	Coumarin **1**	Products **3** and yield[b]
17	 **1q**	 **3q** 55%

[a] Reaction conditions: coumarin (0.5 mmol), CF_3SO_2Na (1.5 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (2.0 mmol) in HOAc (10 mL), 25 °C, 24 h. [b] Isolated yield. [c] Detected by LC-MS.



Scheme 3

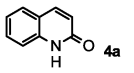
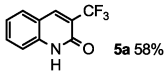
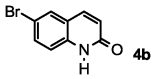
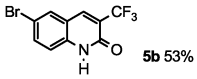
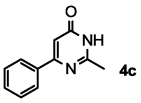
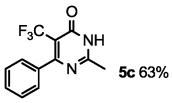
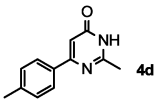
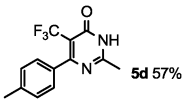
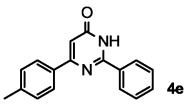
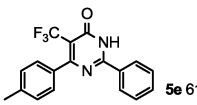
groups like Cl and NO_2 on the phenyl ring gave the products in good yields (up to 70%) (Table 2, entries 8–11). In addition, the electronic and steric effects of the 4-substituent of coumarins were explored, this revealed that both of them played a less significant role in the reaction (Table 2, entries 12–17).

A mechanism for the reaction of coumarins (**1**) with CF_3SO_2Na (**2**) is proposed in Scheme 3. Trifluoromethyl radical **6** derived from **2** is selectively added to the 3-position of **1** to form intermediate radical **7**, which is oxidized by $Mn(OAc)_3$ to form carbocation **8**, and deprotonation of **8** gives product **3**.

We extended this method to other heteroarenes such as 2-quinolinone derivatives **4a** and **4b**, as expected, the CF_3 radical was selectively added to the 3-position of **4a** and **4b** to afford 3-trifluoromethyl quinolinone-2 (**5a** and **5b**) in 58% and 53% yields, respectively (Table 3, entries 1 and 2). Furthermore, when pyrimidinones (**4c–4e**) were exploited for the reaction, 5-trifluoromethyl pyrimidinones (**5c–5e**) were obtained in 57–63% yields (Table 3, entries 3–5).

In conclusion, a novel method for direct C_{sp2}–H radical trifluoromethylation of coumarins was developed through the reaction of sodium trifluoromethanesulfinate (CF_3SO_2Na, Langlois reagent) with coumarins in the presence of $Mn(OAc)_3$. The reaction proceeded under mild conditions in air to afford selective 3-trifluoromethyl coumarins in moderate to good yields, this methodology is straightforward and provides a general, effective and cheap way for the synthesis of 3-trifluoromethyl coumarins and other trifluoromethylated heteroarenes such as 3-trifluoromethyl quinolinone-2 and 5-trifluoromethyl pyrimidinones.

Table 3 Reactions of heteroarene **4** and sodium trifluoromethanesulfinate **2**[a]

Entry	Heteroarene **4**	Product **5** and yield[b]
1	 **4a**	 **5a** 58%
2	 **4b**	 **5b** 53%
3	 **4c**	 **5c** 63%
4	 **4d**	 **5d** 57%
5	 **4e**	 **5e** 61%

[a] Reaction conditions: coumarin (0.5 mmol), CF_3SO_2Na (1.5 mmol) and $Mn(OAc)_3{\cdot}2H_2O$ (2.0 mmol) in HOAc (10 mL), 25 °C, 24 h. [b] Isolated yield.

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