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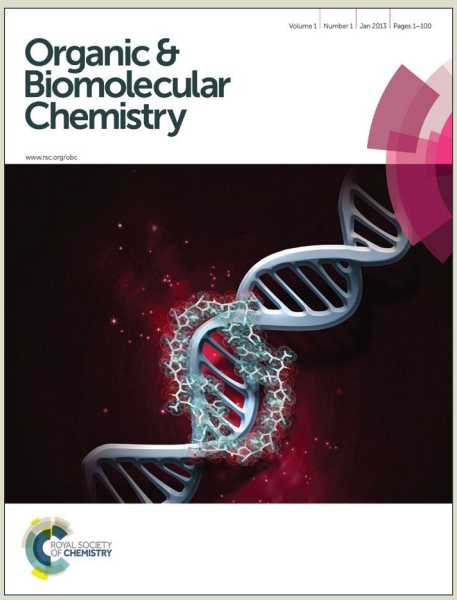

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Copper-Catalysed Ring-Opening Trifluoromethylation of Cyclopropanols†

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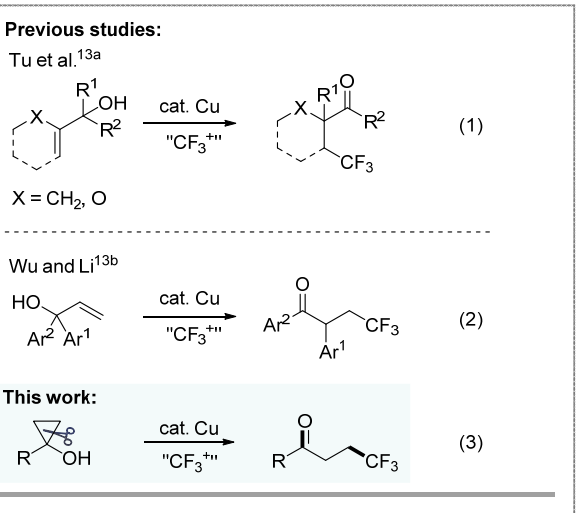
Copper-catalysed ring-opening trifluoromethylation reaction of cyclopropanols has been developed. Various β-trifluoromethyl ketones are obtained in good to excellent yields under mild reaction conditions. The present method also exhibits good functional-group compatibility. The mechanism of this new ring-opening trifluoromethylation reaction was investigated by radical trapping reactions.

The trifluoromethyl (CF_3) group is an important structural motif in many medicinally and biologically important compounds.[1] Thus, considerable attention has been paid to the development of efficient methods for the introduction of CF_3 group into molecules in recent years.[2] In comparison with the significant progress achieved in C(sp^2)-CF_3 and C(sp)-CF_3 bond formation,[3,4] the construction of C(sp^3)-CF_3 is relatively less investigated. Recent advances in this field focus on: (1) the conversion of prefunctionalized alkyl halides,[5] silane[6] and boronic acid[7] to the corresponding C(sp^3)-CF_3 compounds; (2) trifluoromethylation of alkenes;[8] (3) direct C(sp^3)-H tirfluoromethylation.[9] On the other hand, β-trifluoromethyl ketones are important yet synthetically difficult molecules.[10] Traditional method such as nucleophilic addition of "CF_3^-" reagent to enones suffers from the poor regioselectivity.[11] To solve these problems, recent attention has been directed to the use of "CF_3^+" reagent combing with transition metal via a radical process. For example, Shibata et al. recently reported copper-mediated conjugate addition trifluoromethylation of α,β-unsaturated ketones with the Umemoto type "CF_3^+" reagent.[12] Recent breakthroughs for the construction of β-trifluoromethyl ketones have been achieved by rearrangement trifluoromethylation reactions involving C-C bond cleavage.[13] For instance, Tu et al. described the semipinacol rearrangement trifluoromethylation of allylic alcohols (Scheme 1, eq. 1). Wu and Li also reported neophyl rearrangement trifluoromethylation of α,α-diaryl allylic alcohols (Scheme 1, eq. 2). Despite these important advances, it remains important to develop new methodology for the formation of CF_3-containing compounds using C-C bond cleavage strategy.[14]



Scheme 1 The formation of β-trifluoromethyl ketones involving C-C bond cleavage strategy.

Cyclopropanols are easily prepared with the development of Kulinkovich reaction.[15] Importantly, cyclopropanols can undergo synthetically useful ring-opening transformations for the formation of β-substituent (e.g., halogen, aryl, alkyl etc.) ketones.[16] In this context, we are interested in the construction of β-trifluoromethyl ketones from cyclopropanols. From the hypothesis that the ring-opening trifluoromethylation of cyclopropanols would not only expands the concept and utility of C-C bond cleavage trifluoromethylation, but also enable the development of a facile and new route to the synthesis of β-trifluoromethyl ketones, we herein report the copper-catalysed trifluoromethylation reaction of cyclopropanols (Scheme 1, eq. 3). Moreover, our study also adds a new example of cyclopropanols transformation chemistry.

We started our investigations using **1a** as the probe substrate in the presence of a catalytic amount of CuI (20 mmol %) and Togni reagent **2a** in MeOH at 60 °C (Table 1, entry 1). To our surprise, the

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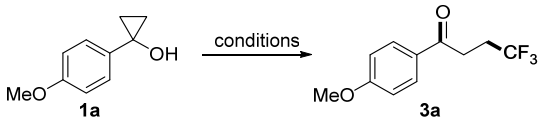
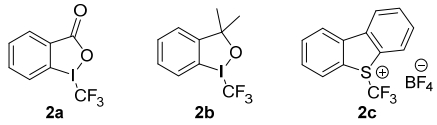
Table 1 Optimization of the reaction conditions[a]

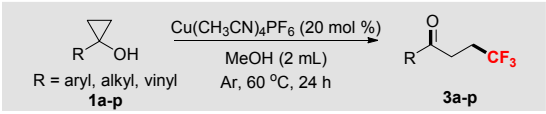


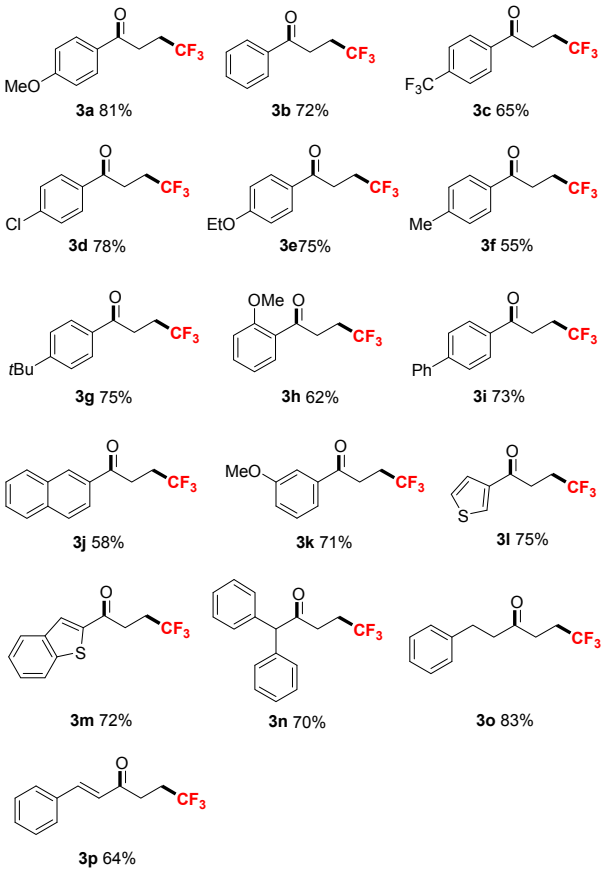
Entry	Copper catalyst	Temp (°C)	Solvent	Time (h)	Yield (%)[b]
1	CuI	60	MeOH	24	25
2	CuTc	60	MeOH	24	29
3	CuCl	60	MeOH	24	65
4	CuBr	60	MeOH	24	60
5	CuSCN	60	MeOH	24	trace
6	$Cu(PP_3)_3Br$	60	MeOH	24	trace
7	**$Cu(CH_3CN)_4PF_6$**	**60**	**MeOH**	**24**	**82**
8[c]	$Cu(CH_3CN)_4PF_6$	60	MeOH	24	59
9[d]	$Cu(CH_3CN)_4PF_6$	60	MeOH	24	50
10	$Cu(CH_3CN)_4PF_6$	60	DMA	24	39
11	$Cu(CH_3CN)_4PF_6$	60	NMP	24	34
12	$Cu(CH_3CN)_4PF_6$	60	DMSO	24	trace
13	$Cu(CH_3CN)_4PF_6$	60	CH_3CN	24	29
14	$Cu(CH_3CN)_4PF_6$	60	1,4-dioxane	24	59
15	$Cu(CH_3CN)_4PF_6$	60	MeOH	12	48
16	$Cu(CH_3CN)_4PF_6$	40	MeOH	24	50
17	none	60	MeOH	24	NR



[a] Unless otherwise noted, the reaction was conducted with **1a** (0.2 mmol), Togni reagent **2a** (1.5 equiv), copper catalyst (20 mol %), MeOH (2 mL) under argon atmosphere, 60 °C, 24 h. [b] Yields were determined by ^{19}F NMR spectroscopy with trifluoromethoxybenzene as an internal standard. [c] Togni reagent **2b** was used. [d] Umemoto reagent **2c** was used. DMA = N,N-dimethylacetamide, NMP = N-methyl-2-pyrrolidone, DMSO = dimethyl sulfoxide. NR = No reaction.

Table 2 Substrate scope of cyclopropanols[a,b]





[a] Reaction conditions: **1** (0.2 mmol), $Cu(CH_3CN)_4PF_6$ (20 mol %), Togni reagent **2a** (1.5 equiv), and MeOH (2 mL) under argon atmosphere, 60 °C, 24 h. [b] Yields of isolated products are shown.

β-trifluoromethyl ketone **3a** was directly formed in 25% yield. Testing of different copper catalysts showed that $Cu(CH_3CN)_4PF_6$ can dramatically improve the yield of **3a** to 82% (Table 1, entry 7). The reaction was also effective with the use of Togni reagent **2b** and Umemoto reagent **2c**, providing the desired product **3a** in 59% and 50% yield, respectively (Table 1, entries 8 and 9). However, when the reaction was conducted in other solvents such as DMA, NMP, DMSO, CH_3CN, or 1,4-dioxane the yields of **3a** were inferior (Table 1, entries 10-14). We also noted that the reaction was not progressing effectively at lower reaction temperature or for shorter reaction time, presumably due to the incomplete conversion of **1a** (Table 1, entries 15 and 16). Finally, it is important to mention that the control experiment conducted in the absence of copper catalyst gave no desired product of **3a** (Table 1, entry 17).

Having optimized the reaction conditions, we next studied the scope of the copper catalysed ring-opening trifluoromethylation of cyclopropanols, and the results are summarized in Table 2. We found that a variety of cyclopropanols can be converted to the desired product in good to excellent yields. The present reaction can tolerate well electron-donating groups such as alkyl (**3f**, **3g**), ether (**3a**, **3e**, **3h**) as well as electron-withdrawing groups such as trifluoromethyl (**3c**), phenyl (**3i**). Notably, this reaction can also tolerate well aryl halide groups such as Cl (**3d**), enabling additional functional handle at these positions via transition-metal-catalysed cross-coupling techniques.[17] Remarkably, pharmaceutically interesting heterocyclic substrates (**3l**, **3m**) were found to be compatible in this reaction, and gave the trifluoromethyl-containing ketones with synthetically useful yields. Importantly, we found that the ring-opening trifluoromethylation of **3p** could be conducted without noticeable ring expansion product.[15g] Finally, aliphatic substituted cyclopropanols were also applicable to give corresponding compounds in good yields (**3n**, **3o**).

To test this newly developed copper-catalysed ring-opening trifluoromethylation methodology in a pharmaceutical context as well as preparative organic synthesis, a drug molecule ibuprofen **4** that contains C–COOH site was converted to the corresponding β-trifluoromethyl ketone. As shown in Fig. 1, ibuprofen **4** can be easily

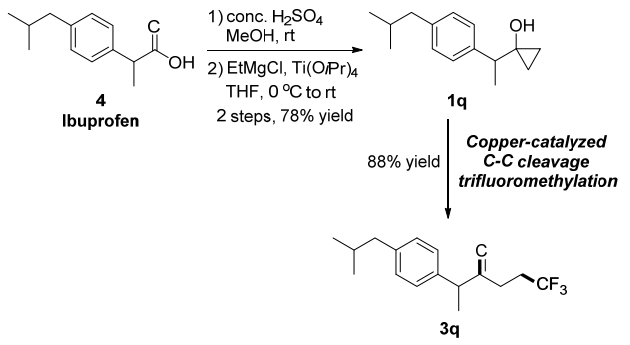


Fig. 1 Application of the copper-catalysed ring-opening trifluoromethylation protocol to pharmaceutically relevant molecule.

converted to the corresponding cyclopropanol **1q** in two steps: acid-catalysed esterification and Kulinkovich reaction.[16] By using the new reaction described in the present study, **1q** can be converted to **3q** in 88% yield.

Note that ketones are known to undergo diverse transformations. We considered that the present reaction combined with further functional group conversions could provide new opportunity for the introduction of CF_3 group into the organic molecules to produce potentially useful building blocks in the field of medicinal chemistry. For example, the CF_3-containing alcohol **5** formed from **3e** in good yields (Fig. 2).

Next, we carried out control experiments to gain more insights

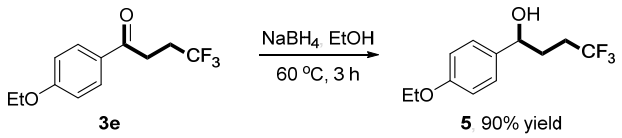
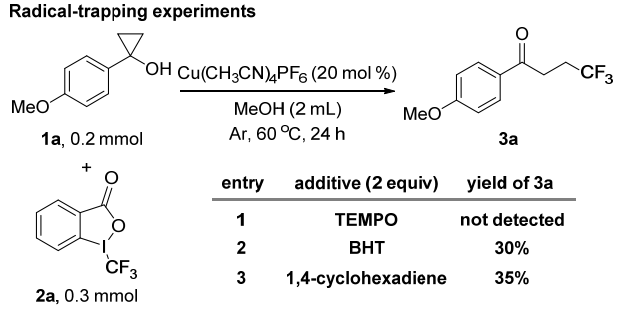


Fig. 2 The reduction of ketone group of **3e**.

on the reaction mechanism (Fig. 3). When the reaction of **1a** with Togni reagent **2a** was conducted in the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO; 2 equiv) under standard conditions, no desired product of **3a** was detected. With the use of other radical inhibitors such as butylated hydroxytoluene (BHT), 1,4-cyclohexadiene, the formation of **3a** was also obviously inhibited. The results of these control experiments suggested that radical is likely involved as the reactive species under the current conditions.



entry	additive (2 equiv)	yield of 3a
1	TEMPO	not detected
2	BHT	30%
3	1,4-cyclohexadiene	35%

Fig. 3 Radical-trapping experiments.

Conclusions

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In summary, we have developed the ring-opening trifluoromethylation of cyclopropanols using $Cu(CH_3CN)_4PF_6$ and Togni reagent **2a** under mild reaction conditions.[18] A wide variety of synthetically useful β-trifluoromethyl ketones were obtained. Further investigations of this reaction system are currently underway in our laboratory.

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