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Copper-Catalyzed Direct C–H Trifluoromethylation of Quinones

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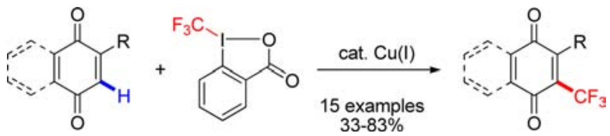
ABSTRACT



An efficient and practical methodology has been developed to introduce the CF_3 group onto quinones through Cu(I)-catalyzed direct C–H trifluoromethylation of quinones.

Quinones can transfer electrons and protons and, thus, behave like redox centers.[1] Many natural products contain quinone subunits.[2] Moreover, molecules bearing a quinone framework have been widely applied in the realm of material sciences, pharmaceuticals, and biochemistry.[2] Quinone derivatives are also used as versatile oxidizing reagents, ligands, and synthons in organic synthesis.[3]

On the other hand, the trifluoromethyl group is valuable in the fields of pharmaceuticals, agrochemicals, and material sciences.[4] Due to the unique properties of CF_3-containing compounds including high electronegativity, lipophilicity, metabolic stability, and bioavailability, it is highly significant to develop efficient methods to introduce the trifluoromethyl group onto organic molecules.[5] The traditional pathway to CF_3-bearing building blocks is a Swarts-type process, which requires exhaustive chlorination, followed by chlorine/fluorine exchange under harsh reaction conditions.[6] Modern trifluoromethylation strategies are based on transition-metal-catalyzed or -mediated cross-coupling reactions[5,7] and radical trifluoromethylations.[8,9]

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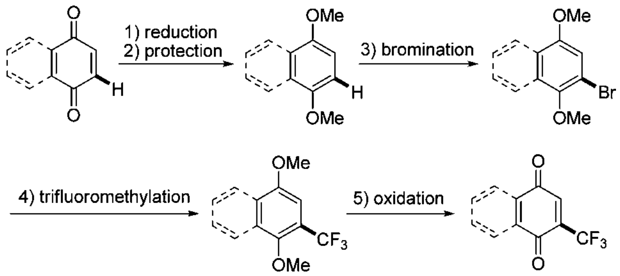
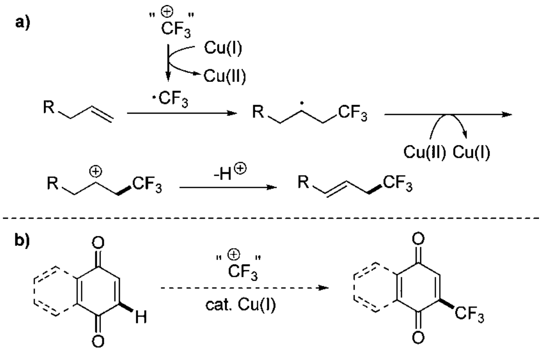
Although remarkable progress has been made on the trifluoromethylation of various types of organic compounds, methods that introduce the CF_3 group onto quinones are still very limited. The few reported methods currently available for CF_3-containing quinone synthesis all need multiple synthetic steps, which usually include reduction, protection, bromination, trifluoromethylation, and deprotection/oxidation (Scheme 1).[10] To the best of our knowledge, direct C−H trifluoromethylation of quinones is not known in the literature.

Scheme 1. Known Method for Trifluoromethylation of Quinone



An interesting recent development in radical trifluoromethylation is that electrophilic trifluoromethylation reagents (CF_3^+) undergo single-electron-transfer (SET) reduction by a Cu(I) catalyst, followed by a radical process and then back electron transfer to regenerate the Cu(I) catalyst. This type of Cu(I)-catalyzed process has been initially applied to allylic trifluoromethylation of olefins using electrophilic trifluoromethylation reagents (Togni reagent and Umemoto regent), reported by Buchwald,[11] Liu,[12] and our group[13] (Scheme 2a), although a different reaction mechanism may operate. Following these reports, various metal-catalyzed trifluoromethylation reactions or related reactions with electrophilic trifluoromethylation reagents have been documented.[14] In all these reports, the trifluoromethyl radical adds to an electron-rich double bond. Inspired by the radical trifluoromethylation of heteroarenes recently reported by MacMillan[9a] and Baran,[9b,d] in which the CF_3 radical also adds to electron-deficient hetero aromatic systems, we conceived that the CF_3 radical may also add to electron-deficient double bond of quinones. Herein we report that the catalytic trifluoromethylation shown in Scheme 2a indeed works with quinones. This transformation represents the first catalytic direct trifluoromethylation of quinones (Scheme 2b).[15]

Scheme 2. Direct C−H Trifluoromethylation of Quinones



At the outset of this investigation, vitamin K **1a** was used as the substrate to screen the reaction conditions for possible direct C−H trifluoromethylation. A trace amount of trifluoromethylated product **3a** was detected by treatment of **1a** with Togni reagent **2a**[16,17] in the presence of 20 mol % of CuCl in MeOH at 80 °C (Table 1, entry 1). After preliminary solvent screening (Table 1, entries 2−6), we identified that the reaction in *t*-BuOH at rt afforded the desired product in 72% GC yield (Table 1, entry 6). We also examined mixed solvents (Table 1, entries 7−9), and the conversion was slightly improved using a solvent mixture of *t*-BuOH/DCM (1:1, v/v)(Table 1, entry 8). A range of temperature was then screened. The yield could be further increased at elevated temperature (Table 1,

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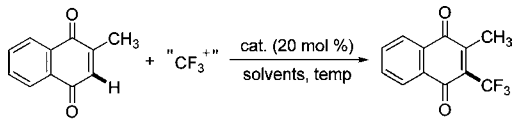
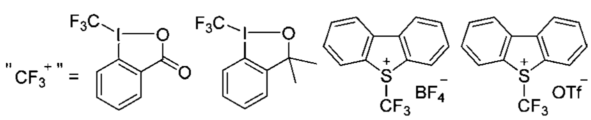
Table 1. Optimization of Direct C−H Trifluoromethylation of Quinone[a]



1a 2 3a

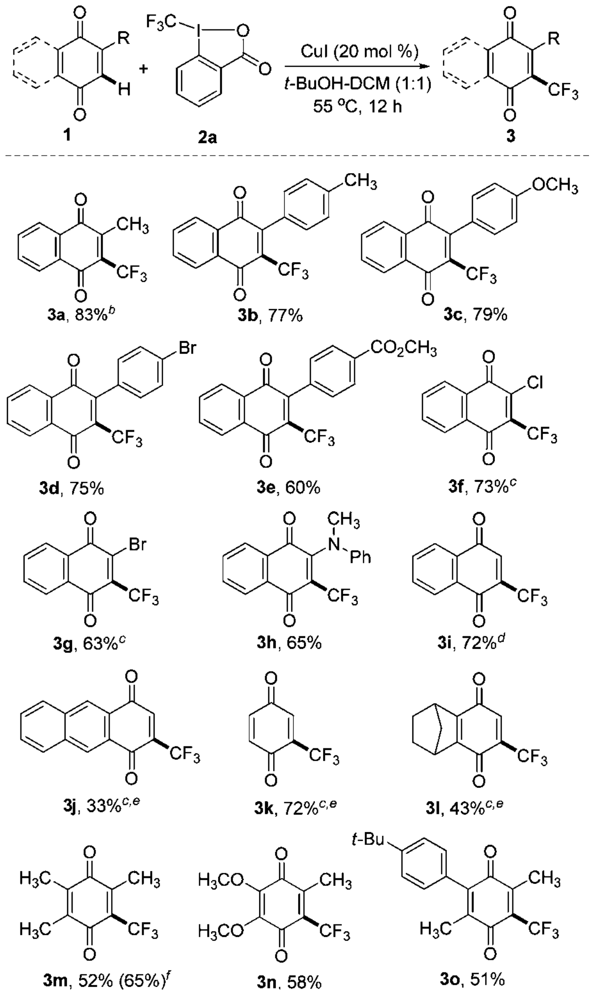
entry	cat.	$^{+}CF_3$	solvent	t (°C)	yield[b]
1	CuCl	**2a**	MeOH	80	trace
2	CuCl	**2a**	DMF	25	trace
3	CuCl	**2a**	DCM	25	58%
4	CuCl	**2a**	*i*-PrOH	25	29%
5	CuCl	**2a**	2-methyl-2-butanol	25	64%
6	CuCl	**2a**	*t*-BuOH	25	72%
7	CuCl	**2a**	*t*-BuOH/CH_2Cl_2 (3:1)	25	71%
8	CuCl	**2a**	*t*-BuOH/CH_2Cl_2 (1:1)	25	74%
9	CuCl	**2a**	*t*-BuOH/CH_2Cl_2 (1:3)	25	59%
10	CuCl	**2a**	*t*-BuOH/CH_2Cl_2 (1:1)	55	79%
11	CuCl	**2a**	*t*-BuOH/CH_2Cl_2 (1:1)	75	80%
12	**CuI**	**2a**	***t*-BuOH/CH_2Cl_2 (1:1)**	**55**	**84%**[c]
13	CuI	**2b**	*t*-BuOH/CH_2Cl_2 (1:1)	55	72%
14	CuI	**2c**	*t*-BuOH/CH_2Cl_2 (1:1)	55	no
15	CuI	**2d**	*t*-BuOH/CH_2Cl_2 (1:1)	55	no
16	CuTc[d]	**2c**	*t*-BuOH/CH_2Cl_2 (1:1)	55	trace
17	CuTc	**2d**	*t*-BuOH/CH_2Cl_2 (1:1)	55	trace
18	$CuCl_2$	**2a**	*t*-BuOH/CH_2Cl_2 (1:1)	55	40%
19	–	**2a**	*t*-BuOH/CH_2Cl_2 (1:1)	55	trace

[a] Reaction conditions: quinone (0.2 mmol, 1.0 equiv), electrophilic trifluoromethylation reagent (0.4 mmol, 2.0 equiv), catalyst (20 mol %), solvent (1 mL), 12 h. [b] GC yield. [c] The isolated yield is 83%. [d] CuTc = (thiophene-2-carbonyloxy)copper.



2a 2b 2c 2d

Scheme 3. Direct C−H Trifluoromethylation of Quinones[a]



[a] Reaction conditions: quinone **1** (0.2 mmol, 1.0 equiv), **2a** (0.4 mmol, 2.0 equiv), CuI (20 mol %), *t*-BuOH−CH_2Cl_2 (1:1, v/v,1.0 mL), 55 °C, 12 h. [b] Isolated yield. [c] Based on ^{19}F NMR analysis using 4-CF_3O-$C_6H_4OCF_3$ as an internal standard. [d] Quinone **1** (0.4 mmol, 2.0 equiv), **2a** (0.2 mmol, 1.0 equiv). [e] quinone **1** (0.5 mmol, 2.5 equiv), **2a** (0.2 mmol, 1.0 equiv). [f] 50 mol % CuI was used.

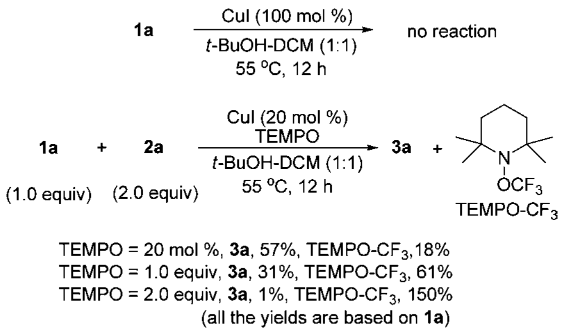
entries 10, 11). **3a** could be obtained in 84% isolated yield when CuI was employed instead of CuCl, and no hydroquinone byproducts were detected (Table 1, entry 12). Replacing **2a** with **2b** led to a slight decline in the yield (Table 1, entry 13). The reaction was totally shut down when CuI/Umemoto reagent **2c** or CuI/Umemoto reagent **2d** was used (Table 1, entries 14, 15). A trace product was observed by using CuTc/Umemoto reagent **2c** and CuTc/Umemoto reagent **2d** (Table 1, entries 16, 17). Finally, $CuCl_2$ only showed moderate efficiency (Table 1, entry18), and a control experiment showed that a copper catalyst was necessary in this reaction (Table 1, entry 19).

With the optimized reaction conditions in hand, we then proceeded to study the scope of this reaction. As shown in Scheme 3, a number of quinone derivatives underwent smooth trifluoromethylation under optimal conditions. High reactivity was observed with naphthoquinones bearing either electron-rich or -deficient arene substituents (**3b**−**e**). The sensitive chlorine and bromine at the β-position of naphthoquinone, which would be vulnerable in Pd-catalyzed transformations, was compatible with the reaction conditions. These halide functional groups are valuable because they can be used in further transformations. Notably, naphthoquinone bearing a *N*-methyl aniline substituent also worked well, providing **3h** in decent yield.

The yield of **3i** was based on **2a**, and excess 1,4-naphthoquinone was necessary to avoid further trifluoromethylation of product **3i**. 1,4-Anthraquinone **1j** exhibited low efficiency due to its low solubility. Monotrifluoromethylated benzoquinone **3k** was obtained in 72% yield (based ^{19}F NMR analysis). Benzoquinone fused with an aliphatic ring also reacted successfully with **2a** to give **3l** in acceptable yield. Trifluoromethylation of trimethylbenzoquinone showed moderate efficiency and yielded **3m** in 52% yield. The yield of **3m** could be increased to 65% with a high catalyst loading (50%). Benzoquinones bearing methoxy and aryl groups were also employed, affording corresponding trifluoromethyl products **3n** and **3o** in moderate yield, respectively.

To gain insight into the reaction mechanism, we have designed a series of experiments (Scheme 4). First, we

Scheme 4. Experiments for Mechanistic Study



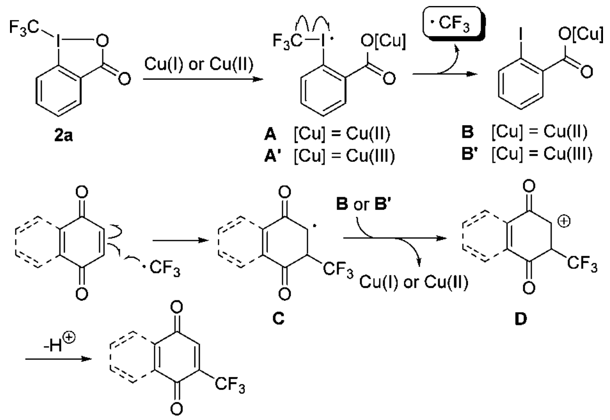
found that no reaction occurred when **1a** was treated with stoichiometric CuI in the absence of Togni reagent **2a**, which indicates that CuI cannot be oxidized by the quinone substrates. In order to probe possible radical intermediates, the trifluoromethylation reaction was then conducted under the standard conditions in the presence of different amounts of radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy).[13] When adding 20 mol % TEMPO, **3a** was diminished to 57% yield (^{19}F NMR), while the TEMPO–CF_3 adduct was formed in 18% yield as estimated by ^{19}F NMR analysis. In the presence of 1.0 equiv of TEMPO, the ^{19}F NMR yield of **3a** was further decreased to 31%, while the TEMPO–CF_3 adduct yield increased to 61%. The reaction was almost shut down by adding 2.0 equiv of TEMPO. However, no TEMPO–quinone adducts were detected in these experiments.

Furthermore, acid catalysts, including $BF_3 \cdot Et_2O$, $AuCl_3$, $TiCl_4$, $FeCl_3$, and CF_3CO_2H (TFA), were employed in this reaction instead of CuI. $TiCl_4$ and $FeCl_3$ achieved the conversion, giving **3a** in 15% and 31% ^{19}F NMR yield, respectively. Only trace **3a** was observed by using $BF_3 \cdot Et_2O$, $AuCl_3$, and TFA. These results indicate that CuI does not act as a nonredox acid catalyst to activate the substrates.

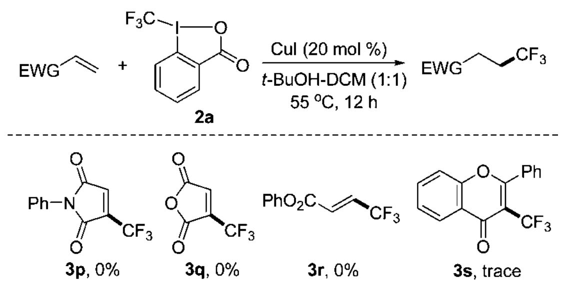
Based on these observations, we considered that the CF_3 radical is involved in the transformation (Scheme 5). At first, Togni reagent **2a** is activated by CuI, generating radical intermediate **A**. Further decomposition of **A** affords Cu(II) species **B** with simultaneous release of the CF_3 radical. Notably, it is possible that resulting Cu(II) species **B** undergoes a second SET oxidation by **2a** to produce radical intermediate **A′**. The collapse of **A′** produces the CF_3 radical and Cu(III) complex **B′**. The putative process is consistent with the fact that the reaction is not quenched by catalytic TEMPO and that Cu(II) also catalyzes this transformation (Table1, entry 18). The CF_3 radical then undergoes addition to quinone to give radical **C**. Oxidation of the radical **C** regenerates active Cu(I) or Cu(II) species and forms carbon cation **D**, which is followed by deprotonation to complete the trifluoromethylation process.

Finally, we conceived that this trifluoromethylation reaction might also be applied to other electron-deficient double bonds (Scheme 6). However, none of them affords

Scheme 5. Mechanistic Rationale



Scheme 6. Attempted Trifluoromethylation with Electron-Deficient Double Bond



the expected trifluoromethylation product. Thus, we consider that the success of this quinone trifluoromethylation method is largely attributed to the special structure of quinones.

In summary, we have developed a novel and practical reaction for trifluoromethylated quinone synthesis. In due course, the $C(sp^2)–CF_3$ bond is formed on an electron-deficient π-system under mild conditions. The reaction employs cheap copper iodide as the catalyst and the hypervalent iodine(III) reagent **2a** as both the oxidant and CF_3 source. The direct C–H functionalization streamlines the synthetic routes and has an advantage over previous methods. Further work will focus on the expansion of the substrate scope and in-depth studies to unambiguously establish the reaction mechanism.

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Supporting Information Available. Experimental procedures, characterization data, and NMR spectra of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.