



Short communication

Photoredox-catalyzed perfluoroalkylation of aminoquinolines with hypervalent iodine(III) reagents that contain perfluoroalkanoate

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ARTICLE INFO

Keywords:

Photoredox-catalyzed
Perfluoroalkylation
Aminoquinolines
Hypervalent iodine(III)
Perfluorocarboxylic acid

ABSTRACT

A practical approach for photoredox-catalyzed perfluoroalkylation of aminoquinolines with $C_6F_5I(OCOR_f)_2$ has been developed. In this reaction, pentafluoroiodobenzene can be recovered and further utilized for the synthesis of $C_6F_5I(OCOR_f)_2$. Importantly, this strategy provides a practical access for the application of perfluorocarboxylic acid as the perfluoroalkyl source. A radical pathway mechanism is suggested according to the results of control experiments.

1. Introduction

In the past few decades, the introduction of fluorine-containing groups into organic molecules has achieved much attention because fluorine-containing compounds play an important role in agrochemicals, pharmaceuticals and many other fields [1–3]. Consequently, the development of novel and practical methods for perfluoroalkylation has become increasingly significant in organic synthesis [4–7].

The quinoline framework has obtained significant attention due to its frequent appearance in natural product and pharmaceuticals [8–10]. Therefore, many investigations have been performed using quinoline as a building block for structural functionalization [11–16]. In contrast, the direct perfluoroalkylation of quinoline at C5 position was rarely reported. In 2017, Zhang group achieved an efficient access to fulfill C5-perfluoroalkylation of quinolines using $TMSR_f$ ($TMS = \text{Tri-methylsilane}$) as perfluoroalkylating reagent (Scheme 1a) [11]. Despite this significant progress, expensive perfluoroalkylation reagent and excess additive were used. Due to these pre-requisites, this transformation failed to meet demands of atom economy.

Recently, the commonly used trifluoromethylation reagents are mainly Umemoto's reagent [17], Togni's reagent [18], Shibata's reagent [19], Langlois' reagent [20] and fluoroform-derived $CuCF_3$ [21]. In consideration of the cost and atom economy, a cheaper and more practical perfluoroalkylation reagent should be developed for the synthesis of fluorine-containing compounds. In addition, hypervalent iodine(III) reagents are widely utilized in many kinds of organic reactions [22]. However, the perfluoroalkylation using hypervalent iodine(III) as perfluoroalkylation reagent was rarely achieved. In 2014, Periana demonstrated a selective C–H functionalization of alkane by a

perfluoroarene iodine(III) complex [23]. In 2017, Maruoka reported photoinduced direct C–H difluoromethylation of heteroarenes with hypervalent iodine(III) difluoroacetates [24]. Very recently, the Qing group described a visible-light photoredox decarboxylation of $C_6F_5I(OCOCF_3)_2$ for C–H trifluoromethylation of arenes. In this study, five examples of perfluoroalkylated products were demonstrated [25].

In recent years, photocatalysis has become a useful tool in organic synthesis because of the lower energy consumption and higher atom economy [26–29]. Based on this background, our research interests focus on the C–H functionalization facilitated by photoredox-catalyzed reactions [26,27]. Herein, we demonstrate a photoredox-catalyzed perfluoroalkylation of aminoquinolines using $C_6F_5I(OCOR_f)_2$ as perfluoroalkylation reagent (Scheme 1b). The $C_6F_5I(OCOR_f)_2$ can be easily prepared from perfluorocarboxylic acid and pentafluoroiodobenzene. Compared with other trifluoromethylation reactions, there are two advantages of our method. On the one hand, perfluorocarboxylic acid represents an attractive perfluoroalkylation source due to low cost and easy accessibility. On the other hand, pentafluoroiodobenzene can be recovered after this transformation, which meets the demands of atom economy.

2. Results and discussion

Initially, the perfluoroalkylation reaction between aminoquinoline (1a) and $C_6F_5I(OCOCF_3)_2$ (2a) was performed in MeCN in the presence of $Ru(bpy)_3Cl_2$ (2 mol%) under the radiation of 12 W blue LED. Target product 3a was obtained in 31% yield (Table 1, entry 1). Then, some photoredox catalysts such as $Ru(bpz)_3(PF_6)_2$, $Ru(bpy)_3(PF_6)_2$, $Ru(phen)_3Cl_2$, $Ir(ppy)_3$, $Ir(dtbbpy)(bpy)_2PF_6$, Acr^+-Mes and eosin Y were

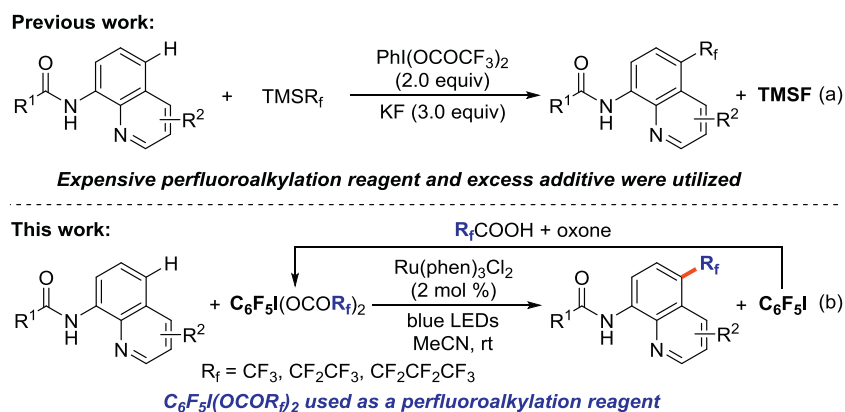
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Received 1 August 2018; Received in revised form 29 August 2018; Accepted 1 October 2018

Available online 10 October 2018

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Scheme 1. Examples of perfluoroalkylation of aminoquinolines.

Table 1
Optimization of reaction conditions^a.

Entry	Photocatalyst	Solvent	Yield [%] ^b
1	Ru(bpy) ₃ Cl ₂	MeCN	31
2	Ru(bpz) ₃ (PF ₆) ₂	MeCN	28
3	Ru(bpy) ₃ (PF ₆) ₂	MeCN	52
4	Ru(phen) ₃ Cl ₂	MeCN	79
5	Ir(ppy) ₃	MeCN	27
6	Ir(dtbbpy)(bpy) ₂ PF ₆	MeCN	42
7	Acr ⁺ – Mes ClO ₄ [–]	MeCN	trace
8	eosin Y	MeCN	trace
9	–	MeCN	0
10 ^c	Ru(phen) ₃ Cl ₂	MeCN	0
11	Ru(phen) ₃ Cl ₂	DMF	trace
12	Ru(phen) ₃ Cl ₂	DCE	trace
13	Ru(phen) ₃ Cl ₂	THF	trace
14 ^d	Ru(phen) ₃ Cl ₂	MeCN	76
15 ^e	Ru(phen) ₃ Cl ₂	MeCN	47
16 ^f	Ru(phen) ₃ Cl ₂	MeCN	trace

Note: bpy = 2,2'-Bipyridine; bpz = 2,2'-Bipyrazine; phen = 1,10-Phenanthroline; ppy = 2-Phenylpyridine; dtbbpy = 4,4'-Bis(1,1-dimethylethyl)-2,2'-bipyridine; Acr⁺ – Mes ClO₄[–] = 9-Mesityl-10-methylacridinium perchlorate; DCE = 1,2-dichloroethane.

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), photocatalyst (0.004 mmol), solvent (2.0 mL), blue LED (12 W), rt., N₂, 12 h.

^b Isolated yields.

^c Without light.

^d KF (0.2 mmol).

^e **2a** (0.2 mmol).

^f Under air.

studied (Table 1, entries 2–8). The product yield increased to 79% when Ru(phen)₃Cl₂ was used as catalyst. Expectedly, no product was generated without photoredox catalysts or light (Table 1, entries 9 and 10). Further investigations on solvent, additive, reaction atmosphere and light source did not improve the yield (Table 1, entries 11–16; see the Supporting Information).

With the optimized reaction conditions in hand, the substrate scope was tested, and the results are shown in Table 2. This perfluoroalkylation reaction demonstrated good functional group tolerance. In general, the yield was decreased from trifluoromethylation to perfluoropropylation because the steric hindrance was increased. The carboxamides with various functional groups afforded target products (**3a–3x**) in moderate to good yields. In addition, aminoquinolines with functional groups (Me and MeO) on quinoline ring were also studied and demonstrated good reactivity, giving the desired products (**3y–3ad**) in 70–80% yields. Furthermore, the molecular structure of product **3ad** was proved by X-ray crystallographic analysis (CCDC NO. 1845481)

(Scheme 2).

To demonstrate the synthetic utility of the perfluoroalkylation reactions, the gram-scale synthesis was carried out, affording product **3a**, **3b** and **3c** in 72%, 70% and 65% yield, respectively (Scheme 3). In the meantime, pentafluoroiodobenzene which could be utilized for the synthesis of C₆F₅I(OCOR)₂ was recovered in 69–76% yields. These results revealed that our method has good atom economy, which is valuable in the preparation of fluorine-containing compounds.

To understand the mechanism of the reaction, some control experiments were performed (Scheme 4). First of all, when TEMPO was added as radical inhibitor, this reaction was completely suppressed (Scheme 4a). Simultaneously, the product **4** was formed in the presence of 1,1-diphenylethylene (DPE) (Scheme 4b), suggesting that a radical pathway could be involved in the reaction. No reaction took place under the optimized reaction conditions when *N*-(5-bromoquinolin-8-yl)benzamide (**1z**) was employed as substrate, the substrate **1z** was recovered in 95% yield (Scheme 4c). Furthermore, the

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