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Copper-catalyzed selective C5-H bromination and difluoromethylation of 8-aminoquinoline amides using ethyl bromodifluoroacetate as the bifunctional reagent†

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A simple and effective method for the copper-catalyzed selective C5-H bromination and difluoromethylation of 8-aminoquinoline amides with ethyl bromodifluoroacetate as the bifunctional reagent was developed. The combination of cupric catalyst and alkaline additive results in a C5-bromination reaction, whereas cuprous catalyst combined with silver additive results in the C5-difluoromethylation reaction. This method has a broad substrate scope and allows for easy and convenient access to desired C5-functionalized quinolones with good to excellent yields.

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Introduction

8-Aminoquinoline derivatives have attracted widespread interest over the past decades because the privileged scaffold can be found in a wide variety of important compounds, including natural products,¹ bioactive molecules,² pharmaceuticals,³ agrochemicals,⁴ pesticides,⁵ optoelectronic materials, and fluorescence probe materials.⁶ Moreover, the efficient and reversible coordination to transition metal catalysts, the low cost, and ease of attachment and detachment from most carboxylic acid substrates make the 8-aminoquinoline a widely applicable auxiliary group for proximal C-H functionalization (Fig. 1).^{7–9} However, extensive research on the structural optimization of lead compounds suggests that the introduction of functional groups onto 8-aminoquinoline motifs could enhance their bioactivities, such as antimalarial and antitumor properties.¹⁰ Therefore, the synthesis of substituted 8-aminoquinolines is crucial.

In recent years, direct C-H activation has emerged as an elegant method for the rapid generation of functionalized 8-aminoquinolines due to its mild conditions, atom economy, and high tolerance to various functional groups. Numerous studies have reviewed the regioselective functionalization of 8-aminoquinolines through C-H activation at the positions of C2–C7.¹¹ Since Stahl *et al.*¹² reported the first instance of cuprous-catalyzed chlorination using lithium chloride in an oxygen atmosphere, remote C5-functionalization has garnered

particular interest.¹³ Recent efforts have been focused on C–C,¹⁴ C–N,¹⁵ C–P,¹⁶ C–O,¹⁷ C–S¹⁸ and C–X¹⁹ bond construction through direct C5-H functionalization *via* transition-metal-catalyzed reactions as well as by employing metal-free conditions.

The difluoromethylene group, which can be proposed as the bioisostere of hydroxyl, carbonyl, amino, and sulfhydryl groups, has evolved as an important structural motif in drug research

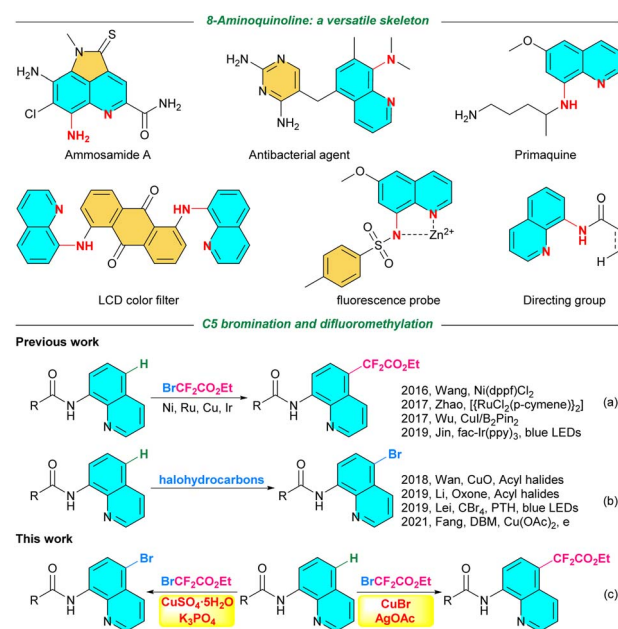


Fig. 1 Synthetic strategies toward C5-brominated and difluoromethylated 8-aminoquinolines and representative 8-aminoquinoline-containing molecules.

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and development. Previous research revealed that bromodifluoroacetates are attractive reagents to incorporate difluoromethylene group due to their post functionalization potential. As illustrated in Fig. 1a, Wang, Zhao, Wu, and Jin, performed the ethoxycarbonyldifluoromethylation of 8-aminoquinolines with the aid of Ni, Ru, Cu, and Ir catalysts through direct C5-H functionalization employing ethyl bromodifluoroacetate as the difluoromethylation reagent.²⁰ These intelligent strategies demonstrated that ethyl difluorobromoacetate is an excellent reagent for introducing the CF₂CO₂Et group on the C5-position of 8-aminoquinolines.

On the other hand, brominated aromatics are important compounds in organic synthesis. To avoid the direct use of hazardous, toxic, and harmful molecular bromine, a large number of efficient brominating reagents and reaction systems for the bromination of arenes in a safe and environmentally friendly manner have been developed. Bromoamide derivatives and other Br-containing chemicals such as HBr, bromine salts, acyl bromides and bromoalkanes have been frequently employed as brominating reagents for the incorporation of the bromine atom into 8-aminoquinolines through direct C5-H functionalization pathway.¹⁹ In addition, the use of halohydrocarbons as brominating reagents has gained traction due to their efficiency, safety, mild reaction conditions, and low pollution. Wan and Li independently reported two methods for the one-pot *N*-acylation and C5-H halogenation of 8-aminoquinolines using acyl halides as the donors of both the acyl and halide atoms. Lei and Fang developed the C5-bromination of 8-aminoquinoline amides using inert halomethanes as the halogen source, utilizing photocatalytic and electrocatalytic technologies (Fig. 1b).²¹ However, to the best of our knowledge, the direct C5-H bromination of 8-aminoquinolines using ethyl difluorobromoacetate as the organic halogen source has not been previously reported. Hence, to address the gap in knowledge, this study presents a simple and efficient method for copper-catalyzed selective C5-H bromination and difluoromethylation of 8-aminoquinoline amides with ethyl bromodifluoroacetate as the bifunctional reagent (Fig. 1c).

Results and discussion

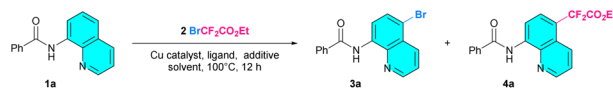
N-(Quinolin-8-yl)benzamide (**1a**, 0.2 mmol) and ethyl bromodifluoroacetate (**2**, 0.8 mmol) were selected as the model substrates for the optimization of reaction conditions, and the results are shown in Table 1. Initially, the reaction was carried out in DMSO (1.0 mL) at 100 °C for 12 h under air in the presence of a catalytic amount of CuCl₂ (20 mol%) using K₂CO₃ as the additive. The result gave *N*-(5-bromoquinolin-8-yl)benzamide (**3a**) rather than ethyl 2-(8-benzamidoquinolin-5-yl)-2,2-difluoroacetate (**4a**) as the only product obtained with a 32% yield (Table 1, entry 1). The catalysts were then extensively screened, resulting in a significant improvement of the yield of the brominated product **3a** to 75% when CuSO₄ was employed, and the reaction yields improved further to 84% when CuSO₄·5H₂O was employed as the catalyst (Table 1, entries 2 and 3). Interestingly, cuprous salts were also capable of promoting the transformation with a significant yield (Table 1,

entry 4). Numerous additives, including Li₂CO₃, Cs₂CO₃, KHCO₃, and K₃PO₄, were investigated, and the experimental results revealed that K₃PO₄ was the most efficient alkaline additive (96%) of the group (Table 1, entries 5–8). In addition, DMF, MeCN, and DCE solvents were also examined; the results were insignificant for the bromination reaction (Table 1, entries 9–11). The effects of some crucial factors, such as the loading of copper catalyst, the dosage of the additive, the amount of ethyl bromodifluoroacetate (**2**), as well as the reaction temperature, were also investigated (Table 1, entries 12–15).

Previous literature suggested that silver salts could be used as single electron oxidants to initiate radical transformations in α -carbonyl alkyl bromide reactions.²² Further investigation of the copper catalyzed C5-difluoromethylation reaction of 8-aminoquinoline amides was carried out employing AgOAc as the additive. Based on the optimal conditions that were established for the C5-bromination, the reaction was carried out in the presence of CuSO₄·5H₂O (50 mol%) in DMSO (1.0 mL) with AgOAc (0.4 mmol) at 100 °C under an N₂ atmosphere for 12 h. This yielded no desired product (**4a**) (Table 1, entry 16). Subsequent screening revealed that CuBr outperformed Cu(OAc)₂ and CuI in terms of activity, and the desired product **4a** was obtained at a 62% yield (Table 1, entries 17–19). Other silver additives like Ag₂O and Ag₂CO₃ could not promote the difluoromethylation reaction (Table 1, entries 20 and 21). Several other solvents, such as DMF, MeCN, THF, and toluene, were examined, but none of them was as effective as DMSO (Table 1, entries 22–25). Then, a series of ligands were also screened; the addition of ligands did not significantly increase the yield of the desired product; however, the loading of the copper catalyst could be decreased to 20 mol% (Table 1, entries 26–30). Contradictory experiments revealed that the yield decreased with decreased amounts of AgOAc, ethyl bromodifluoroacetate (**2**) and the reaction temperature (Table 1, entries 31–33).

With the optimized reaction conditions in hand, these protocols were then applied to a series of 8-aminoquinoline amides, and the results are shown in Fig. 2 and 3. Based on these results, it can be concluded that the present reactions possessed the advantages of broad substrate scopes, mild reaction conditions, moderate to excellent product yields, and remarkable functional group tolerance. Initially, the substrate scope for the C5-bromination reaction was explored (Fig. 2). 8-Aminoquinoline amides with a variety of substituted groups on different positions of benzene rings in the benzoic acid section exhibited high reactivity (**3b–3k**). Aromatic amides with electron-donating substituted groups (Me, OMe, OAc) and electron-withdrawing substituted groups (CF₃, F, Cl, Br, I, CO₂Me, CN) were well tolerated in this reaction, resulting in an 84% to almost quantitative yield. Furthermore, 8-aminoquinoline amide containing multiple methoxyl groups behaved well in the reaction and gave the product **3l** in a 96% yield. Notably, the compatibility with halogen atoms, particularly I, Br, and Cl, enables the brominated products to undergo downstream transformations (**3f–3h**). Moreover, to extend the substrate scope, various aliphatic amides, including phenylacetamide, isopropylamide, and pivalamide, were evaluated and provided



Table 1 Optimization of the copper-catalyzed C5-selective functionalization reaction^a

Entry	Cu catalyst (mol%)	Ligand (mol%)	Additive (mmol)	Solvent	3a yield ^b (%)	4a yield ^b (%)
1	CuCl ₂ (20)	—	K ₂ CO ₃ (0.2)	DMSO	32	—
2	CuSO ₄ (20)	—	K ₂ CO ₃ (0.2)	DMSO	75	—
3	CuSO ₄ ·5H ₂ O (20)	—	K ₂ CO ₃ (0.2)	DMSO	84	—
4	CuCl (20)	—	K ₂ CO ₃ (0.2)	DMSO	78	—
5	CuSO ₄ ·5H ₂ O (20)	—	Li ₂ CO ₃ (0.2)	DMSO	82	—
6	CuSO ₄ ·5H ₂ O (20)	—	CS ₂ CO ₃ (0.2)	DMSO	88	—
7	CuSO ₄ ·5H ₂ O (20)	—	KHCO ₃ (0.2)	DMSO	92	—
8	CuSO₄·5H₂O (20)	—	K₃PO₄ (0.2)	DMSO	96 (93)	—
9	CuSO ₄ ·5H ₂ O (20)	—	K ₃ PO ₄ (0.2)	DMF	5	—
10	CuSO ₄ ·5H ₂ O (20)	—	K ₃ PO ₄ (0.2)	MeCN	—	—
11	CuSO ₄ ·5H ₂ O (20)	—	K ₃ PO ₄ (0.2)	DCE	—	—
12	CuSO ₄ ·5H ₂ O (10)	—	K ₃ PO ₄ (0.2)	DMSO	68	—
13	CuSO ₄ ·5H ₂ O (20)	—	K ₃ PO ₄ (0.1)	DMSO	—	—
14 ^c	CuSO ₄ ·5H ₂ O (20)	—	K ₃ PO ₄ (0.2)	DMSO	81	—
15 ^d	CuSO ₄ ·5H ₂ O (20)	—	K ₃ PO ₄ (0.2)	DMSO	—	—
16	CuSO ₄ ·5H ₂ O (50)	—	AgOAc (0.4)	DMSO	—	—
17	Cu(OAc) ₂ (50)	—	AgOAc (0.4)	DMSO	—	37
18	CuBr (50)	—	AgOAc (0.4)	DMSO	—	62
19	CuI (50)	—	AgOAc (0.4)	DMSO	—	49
20	CuBr (50)	—	Ag ₂ O (0.4)	DMSO	—	—
21	CuBr (50)	—	Ag ₂ CO ₃ (0.4)	DMSO	—	—
22	CuBr (50)	—	AgOAc (0.4)	DMF	—	38
23	CuBr (50)	—	AgOAc (0.4)	MeCN	—	28
24	CuBr (50)	—	AgOAc (0.4)	THF	—	—
25	CuBr (50)	—	AgOAc (0.4)	Toluene	—	—
26	CuBr (50)	TMEDA (100)	AgOAc (0.4)	DMSO	—	43
27	CuBr (50)	AdCO ₂ H (100)	AgOAc (0.4)	DMSO	—	50
28	CuBr (50)	Ac-Gly-OH (100)	AgOAc (0.4)	DMSO	—	66
29	CuBr (20)	Ac-Gly-OH (40)	AgOAc (0.4)	DMSO	—	67 (62)
30	CuBr (10)	Ac-Gly-OH (20)	AgOAc (0.4)	DMSO	—	40
31	CuBr (20)	Ac-Gly-OH (40)	AgOAc (0.2)	DMSO	—	35
32 ^c	CuBr (20)	Ac-Gly-OH (40)	AgOAc (0.4)	DMSO	—	52
33 ^d	CuBr (20)	Ac-Gly-OH (40)	AgOAc (0.4)	DMSO	—	63

^a Reaction conditions: **1a** (0.2 mmol), **2** (0.8 mmol), Cu catalyst, ligand, additive, solvent (1.0 mL). ^b ¹H NMR yield with dibromomethane as the internal standard, isolated yield in parentheses. ^c 0.6 mmol **2** was used. ^d Stirred at 80 °C. TMEDA = *N,N,N',N'*-tetramethylethylenediamine; AdCO₂H = 1-adamantanecarboxylic acid; Ac-Gly-OH = *N*-acetylglycine.

the desired products in good yields (**3m–3o**). In addition, amides with tension rings and polycyclic structures also survived in this reaction, affording the target molecules good to excellent yields (**3p,3q**). Satisfactorily, the methoxy-substituted quinoline at the C6 position was compatible and provided the desired product **3r** in a 92% yield.

Next, the applicability of the C5-difluoromethylation reaction for different 8-aminoquinoline amides was extensively investigated. As listed in Fig. 3, the results clearly show that aromatic amides with a variety of functional groups on the benzene ring as well as different kinds of aliphatic amides were able to accomplish the difluoromethylation reaction with ethyl bromodifluoroacetate (**2**) smoothly, affording the desired coupling products **4a–4ai** in moderate to good yields. The ethoxycarbonyldifluoromethyl group could be introduced onto α,α -difluorophenylacetamide through this reaction to afford the

bis-difluoromethylated product **4y** in 60% yield. In addition, halogen atoms could be preserved integrally in this transformation, although a silver acetate additive was involved (**4k–4p**). Moreover, the substrate with a methoxyl group on the quinoline scaffold proceeded well to afford the difluoromethylated product in a 71% yield (**4aj**).

Finally, to gain a preliminary understanding of these reactions, some extended investigations were performed (Scheme 1). Firstly, we failed to apply this method to *N*-methyl-*N*-(quinolin-8-yl)benzamide (**5**), quinolin-8-yl benzoate (**6**), *N*-(naphthalen-1-yl)benzamide (**7**), 8-aminoquinoline (**8**), and its alkylated derivatives (**9**, **10**). These revealed that the *N,N*-bidentate chelating coordination of the 8-aminoquinoline amide skeleton is necessary. Subsequently, several control experiments were carried out to investigate the mechanisms. It was observed that the bromination reaction continued in the



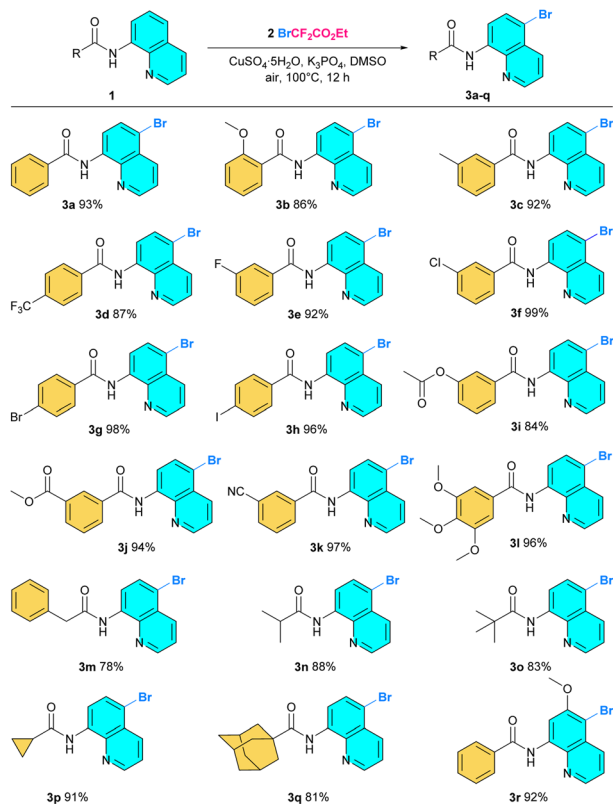


Fig. 2 Substrate scope for the C5-bromination of 8-aminoquinoline amides.

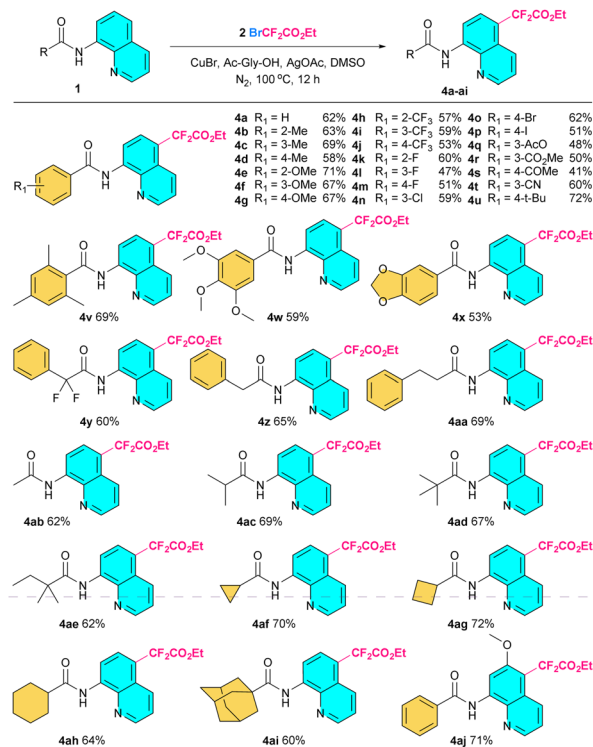
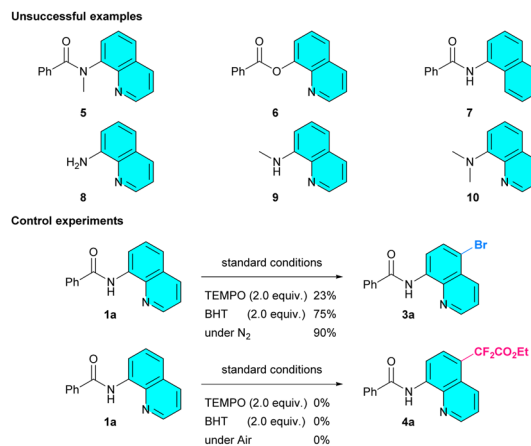


Fig. 3 Substrate scope for the C5-difluoromethylation of 8-aminoquinoline amides.

presence of free radical scavengers such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-tertbutyl-4-methylphenol (BHT), while the difluoromethylation reaction was completely inhibited. In addition, the corresponding product 3a was obtained in 90% yield when the bromination reaction was conducted under nitrogen atmosphere. However, when the difluoromethylation reaction was carried out in an air atmosphere, no product was obtained, and the initial material was recovered. Meanwhile, the TEMPO- $\text{CF}_2\text{CO}_2\text{Et}$ adduct was detected by GC-MS (see ESI[†]). These results indicated that the difluoromethylation might proceed *via* a free radical process and the bromination might be accomplished through an ionic pathway.

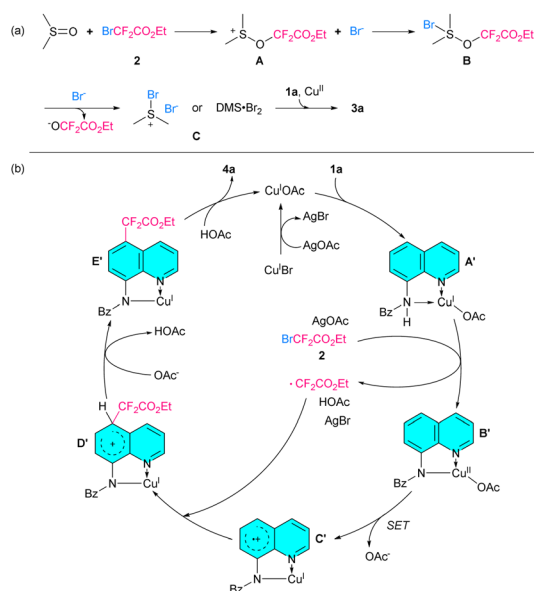
Although the precise mechanisms remain unclear to date, on the basis of our experimental results and literature,²³ plausible mechanisms are proposed. As shown in Scheme 2(a), the nucleophilic attack of DMSO on ethyl bromodifluoroacetate (2) to give intermediate A, which then reacts with the bromine anion to produce intermediate B. Subsequently, dimethylsulfonium bromide or dimethyl thioether/molecular bromine complex C is generated by the attack of the bromine anion on intermediate B.^{23a,b} Finally, bromination is accomplished through the aromatic electrophilic substitution of intermediate C with 1a with the help of copper salt. In Scheme 2(b), a mechanistic hypothesis for the difluoromethylation of 8-



Scheme 1 Extended investigations.

aminoquinoline amide is also proposed. Firstly, CuOAc is provided by the anion exchange of CuBr with AgOAc. The Cu(I)-quinoline complex A' is then formed *via* bidentate nitrogen atom chelation. The intermolecular SET from A' to ethyl bromodifluoroacetate (2) followed by the deprotonation in the presence of AgOAc produces $\cdot\text{CF}_2\text{CO}_2\text{Et}$ radical and the Cu(II) complex B'.^{23c,d} Subsequently, the intramolecular SET process within B' produces a cationic radical C'.^{18g} The radical coupling reaction of C' with $\text{CF}_2\text{CO}_2\text{Et}$ affords the cationic intermediate





Scheme 2 Proposed mechanisms.

D'. The obtained **D'** undergoes deprotonation and demetallation to yield the desired product **4a** as well as the regenerated Cu(i) catalyst for the next catalytic cycle. Further investigation is being conducted to provide evidence for the proposed mechanism.

Conclusions

In summary, we have established a simple and efficient method for copper-catalyzed selective C5-H bromination and difluoromethylation of 8-aminoquinoline amides with ethyl bromodifluoroacetate. The results showed that when cupric catalyst is combined with an alkaline additive, it leads to the C5-bromination reaction while the C5-difluoromethylation reaction is dominant for cuprous catalyst combined with a silver additive. This method has mild reaction conditions, moderate to excellent product yields, and a wide range of substrates. Future investigations will focus on mechanism details and other selective functionalization reactions employing halogenated hydrocarbons as bifunctional reagents.

Experimental

General procedure for the C5-bromination

A 35 mL sealed tube equipped with a stir bar was charged with *N*-(quinolin-8-yl)benzamide (49.6 mg, 0.2 mmol, 1.0 equiv.), BrCF₂CO₂Et (104 μL, 0.8 mmol, 4.0 equiv.), CuSO₄·5H₂O (10.0 mg, 0.04 mmol, 20 mol%), K₃PO₄ (42.5 mg, 0.2 mmol, 1.0 equiv.) and DMSO (1.0 mL). The tube was sealed with a Teflon cap under air, then the mixture was stirred at 100 °C for 12 h. After completion, the reaction mixture was diluted with ethyl acetate (20 mL) and washed successively with saturated sodium bicarbonate, saturated sodium sulfide, and brine. The organic layer was dried over anhydrous sodium sulfate and

concentrated *in vacuo*. The residue was purified on preparative thin layer chromatography (PTLC) to afford the desired product **3a**.

General procedure for the C5-difluoromethylation

A 35 mL Schlenk tube equipped with a stir bar was charged with *N*-(quinolin-8-yl)benzamide (49.6 mg, 0.2 mmol, 1.0 equiv.), CuBr (5.8 mg, 0.04 mmol, 20 mol%), Ac-Gly-OH (9.4 mg, 0.08 mmol, 40 mol%), and AgOAc (67 mg, 0.4 mmol, 2.0 equiv.) under air. The tube was sealed with a rubber stopper and then evacuated and backfilled with N₂ five times. BrCF₂CO₂Et (104 μL, 0.8 mmol, 4.0 equiv.) and DMSO (1.0 mL) were injected *via* syringe. After the reaction was stirred at 100 °C for 12 h, it was allowed to cool to room temperature. The reaction mixture was diluted with ethyl acetate (20 mL) and then washed successively with saturated sodium bicarbonate, saturated sodium sulfide, and brine. The organic layer was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was purified on PTLC to afford the desired product **4a**.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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