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Photoinduced copper-catalyzed alkoxy carbonylation of alkyl fluorides†

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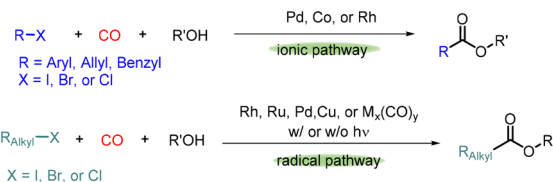
As the strongest σ bond in organic chemistry, the functionalization of the carbon–fluoride bond (BDE = 485 kJ mol^{−1}) remains a significant challenge. Herein, we developed a carbonylation procedure that utilizes a copper catalyst and visible light irradiation to enable the production of esters from alkyl fluorides and phenols for the first time. From our mechanistic studies, the use of magnesium iodide as an additive was found to be crucial for the success of this protocol which drives the halide exchange and removes fluoride from the reaction.

Ester compounds are of great importance as they are found in numerous natural products, pharmaceuticals, polymers, synthetic intermediates, *etc.*¹ Traditionally, esters are mainly synthesized from the esterification between the corresponding carboxylic acid derivatives and alcohols. However, the requirement of strongly alkaline conditions or/and a stoichiometric amount of activators restricts the application of this type of reaction.

On the other hand, using carbon monoxide as a cheap and readily available C1 source, the carbonylation reaction has become a powerful and dominant tool for producing various carbonylated compounds in a highly atom-economical manner.² In this area, the carbonylation reaction of organic halides has received considerable attention since 1963.³ Generally, catalytic methods for carbonylation of organic halides proceed in two possible pathways:⁴ (i) transition metal-catalyzed carbonylation of sp²–X bonds and benzylic halides *via* an ionic pathway (Scheme 1a (1)); Morikawa, Fuchikami, Beller and many other research groups developed various novel protocols for the carbonylation of aryl, allyl, benzyl, and perfluoroalkyl halides with alcohols.⁵ The procedure applicable for alkyl halides is still very limited due to the barrier in oxidative addition and fast β -hydride elimination of the alkyl metal species.⁶ Recently, (ii) radical carbonylation became a new and alternative way to resolve these problems (Scheme 1a (2)).⁷ In 1988, Watanabe and co-workers developed a transition metal carbonyl complex-catalyzed radical carbonylation of alkyl iodide under visible light irradiation.⁸ Subsequently,

Ryu's group reported a visible light-induced Pd-catalyzed radical carbonylation reaction of alkyl iodide with alcohols.⁹ In 2016, Alexanian and co-workers developed a Pd-catalyzed radical alkoxy carbonylation of alkyl bromides using the NHC ligand.^{10a} More recently, Beller's group disclosed the Rh-catalyzed radical carbonylation of primary alkyl chlorides with sodium iodide as the additive.^{10b} Arndtsen and co-workers achieved novel catalytic systems for the carbonylative transformations of organic halides by the combination of a palladium catalyst and visible light.¹¹ In recent years, our group has also been interested in the metal-catalyzed carbonylation of alkyl halides under mild conditions, and various transition metal catalysts (Ru, Rh, Cu, and Fe) were studied.¹² However, for the carbonylation of alkyl fluorides, which have the highest

a) Transition-metal catalyzed alkoxy carbonylation of halides

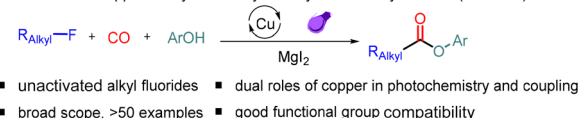


b) The bond dissociation energy (BDE) of alkyl halides

C(sp ³)-F	C(sp ³)-Cl	C(sp ³)-Br	C(sp ³)-I
485 KJ/mol	354 KJ/mol	297 KJ/mol	235 KJ/mol

Relative reactivity: F >> I > Br > Cl

c) Photoinduced copper-catalyzed alkoxy carbonylation of alkyl fluoride (this work)



Scheme 1 Alkoxy carbonylation of alkyl halides.

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bond dissociation energy (485 kJ mol^{-1} ; Scheme 1b),^{13,14} no procedure yet has been reported.

Herein, we present the successful alkoxycarbonylation of alkyl fluorides with phenols under light irradiation catalyzed by a copper catalyst (Scheme 1c). The addition of magnesium iodide was found to be crucial for the success of this transformation, which not only generates more reactive species *in situ* via halogen exchange but also avoids the influence of fluoride ions in the reaction solution on the subsequent radical course. A wide range of valuable esters were produced in high yields with excellent functional group adaptations.

Our initial studies were carried out with 1-fluorooctane (**1a**) and phenol (**2a**) as the model substrates to examine the reaction parameters (Table 1 and also see the ESI, Tables S1–S5†). After a series of studies, we were pleased to find that the desired reaction indeed worked smoothly at 80°C , when employing a catalytic system consisting of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (10 mol%) and Xantphos (11 mol%) in the presence of 2.5 equivalents of K_2CO_3 and 1.5 equivalents of MgI_2 , and the desired product **3a** was formed in 95% NMR yield (Table 1, entry 1). Control experiments, without light irradiation or the use of blue light, confirmed that the reaction proceeded through a photocatalytic process (Table 1, entries 2 and 3). No reaction occurred at room temperature and the alkyl fluoride remained unreacted (Table 1, entry 4). The use of other metal iodides such as LiI and CaI_2 instead of MgI_2 resulted in no reaction despite the detection of 1-iodooctane (Table 1, entries 5 and 6). Notably, the valence of the copper salt is important

for the onset of the reaction as well; Cu^{1+} could initiate the alkoxycarbonylation, whereas no product could be found when Cu^{2+} was used or in the absence of a copper salt (Table 1, entries 7–9). We then investigated other bidentate phosphine ligands and an obvious effect on the yield of the final product was found, with Xantphos still being the best ligand of choice (Table 1, entries 10 and 11). The effects of bases were tested, and poor yields were obtained with either other inorganic bases or organic bases (Table 1, entries 12–14). Moreover, we also found that the reaction appeared to be sensitive to the properties of solvents; a strongly polar solvent completely inhibited the formation of the targeted ester, and a non-polar or weakly polar solvent ensured the proceeding of the desired alkoxycarbonylation, with anisole being the best solvent (Table 1, entries 15 and 16).

With the optimized reaction conditions in hand, we investigated the substrate scope of this reaction, and the results are shown in Scheme 2. At the first stage, a range of phenols with electron-donating groups or electron-withdrawing groups could serve as effective partners, providing the desired esters in good to excellent yields. Versatile functional groups, such as alkyl (**3b–3d**, **3o**), phenyl (**3e**), halogen (**3f–3i**), trifluoromethyl (**3j**), cyano (**3k**), alkoxy (**3l**), alkylthio (**3m**), alkylsulfonyl (**3n**), and Bpin (**3p**), were all tolerated well in the reaction system with high yields. Subsequently, the steric hindrance effect was tested. Phenols with different groups substituted at the *meta*-position were used, and the desired *meta*-substituted phenol esters were obtained (**3q–3s**). Phenols bearing *ortho*-substituents gave the desired esters in moderate to good yields as well irrespective of the steric hindrance effect (**3t–3w**). Furthermore, phenols possessing di-substituents still reacted well and gave the products in good yields (**3x–3z**, **4a**, and **4b**). The natural product sesamol can give the corresponding product with excellent yield in this reaction (**4c**). Next, we investigated the reaction with naphthols, and 2-naphthol gave a better yield than 1-naphthol (**4d** and **4e**). Aliphatic alcohol was also tested but was proven to be an unsuitable reaction partner, which gave the corresponding product in only 22% yield (**4f**). Remarkably, an interesting product was formed when we used 4-hydroxybenzyl alcohol as the substrate. The 4-hydroxybenzyl alcohol reacted with anisole first through electrophilic aromatic substitution,¹⁵ and then alkoxycarbonylation occurred to give the final product (**4g**) in 80% yield.

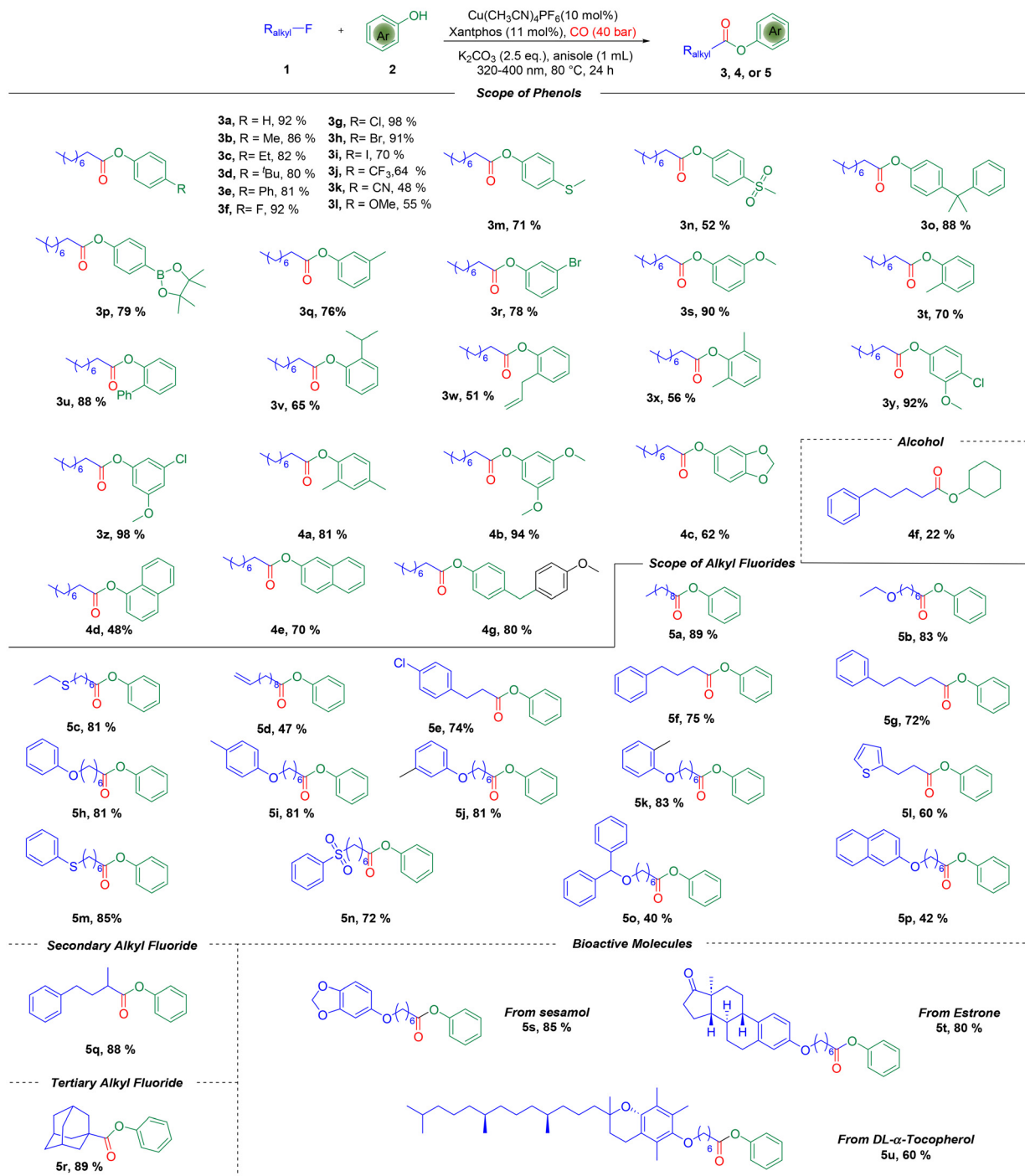
Subsequently, the scope of different types of alkyl fluorides was examined (**5a–5u**). The alkyl fluoride with a long carbon chain also gave an excellent yield (**5a**), and functional groups such as ether (**5b**), thioether (**5c**), alkenyl (**5d**), and alkyl groups (**5e–5g**) were all well tolerated. Phenoxy fluorides with different substituents also gave excellent yields (**5h–5k**). Meanwhile, heterocycle (**5l**), phenylthio (**5m**), phenylsulfonyl (**5n**), and naphthylthio (**5p**) groups were all compatible under the standard conditions to give the desired esters in moderate to good yields. It is noteworthy that the reaction was also extended to the alkoxycarbonylation of secondary and tertiary alkyl fluorides, with the corresponding esters being delivered smoothly (**5q** and **5r**). Importantly, the alkoxycarbonylation

Table 1 Optimization of the reaction conditions^a

Entry	Deviation from standard conditions	3a yield (%)
1	None	95 (92) ^b
2	No light	0
3	Blue light	0
4	r.t.	0
5	LiI instead of MgI_2	0
6	CaI_2 instead of MgI_2	0
7	No $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	0
8	CuI instead of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	15
9	$\text{Cu}(\text{OAc})_2$ instead of $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$	0
10	BINAP instead of Xantphos	<5
11	Niphos instead of Xantphos	16
12	Na_2CO_3 instead of K_2CO_3	<5
13	Cs_2CO_3 instead of K_2CO_3	33
14	DBU instead of K_2CO_3	0
15	CH_3CN as solvent	0
16	Toluene as solvent	58

^a Standard conditions: **1a** (0.2 mmol, 2.0 eq.), **2a** (0.1 mmol, 1.0 eq.), MgI_2 (0.15 mmol, 1.5 eq.), $\text{Cu}(\text{CH}_3\text{CN})_4\text{PF}_6$ (10 mol%), Xantphos (11 mol%), K_2CO_3 (0.25 mmol, 2.5 eq.), CO (40 bar), anisole (1 mL), stirred at 80°C for 24 h under irradiation (320–400 nm); yields were determined by ^1H NMR with 1,3,5-trimethoxybenzene as the internal standard. ^b Isolated yield.





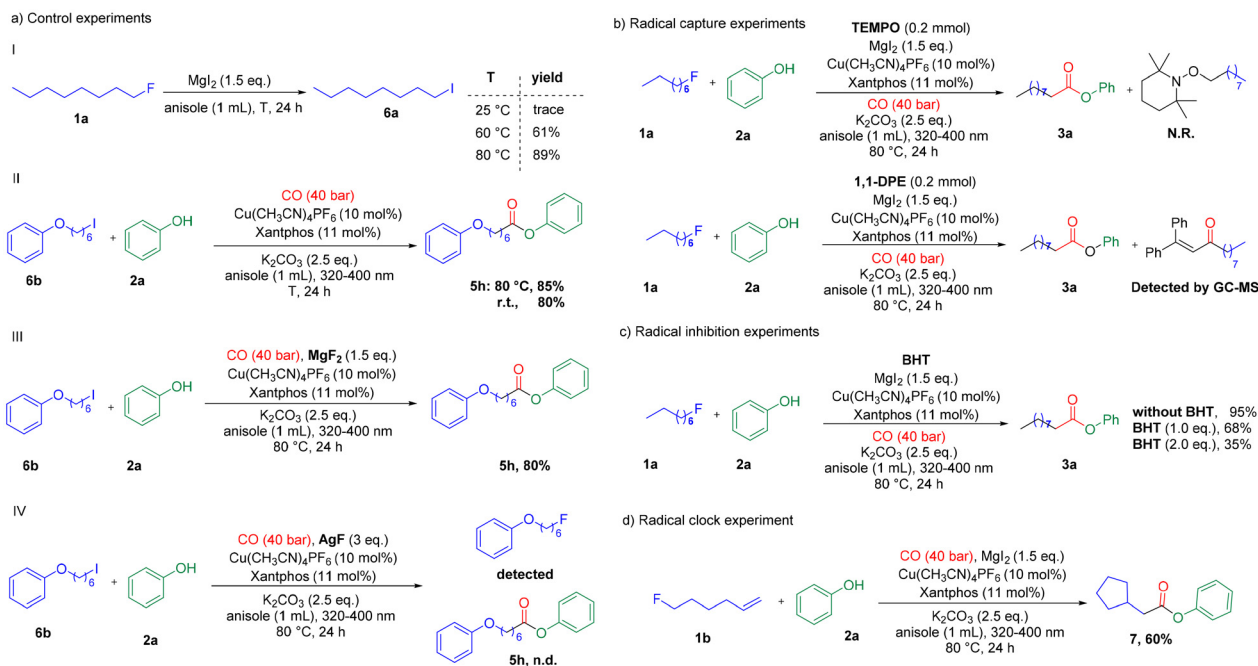
Scheme 2 Reaction scope. Reaction conditions: alkyl fluorides **1** (0.2 mmol, 2eq.), phenols **2** (0.1 mmol, 1.0 eq.), Cu(CH₃CN)₄PF₆ (10 mol%), Xantphos (11 mol%), MgI₂ (1.5 eq.), K₂CO₃ (2.5 eq.), anisole (1 mL), CO (40 bar), 80 °C, irradiation (320–400 nm), 24 h.

can incorporate an ester fragment into natural products, while the alkyl fluoride derivatives from sesamol, estrone, and DL- α -tocopherol could also be converted into the corresponding alkoxyacylation products in 60–85% yields (**5s–5u**).

Control studies were also carried out to explore the reaction mechanism. At first, we studied the conversion of alkyl fluoride to alkyl iodide, and the fluoride/iodide exchange reaction

proceeded with an excellent yield at 80 °C (Scheme 3a–I). To gain more insight into the mechanism and to identify the rate-determining step of the reaction, we studied the kinetic profile of the halogen exchange reaction. As shown in Fig. 1, in the first 2 h, 70% of 1-fluorooctane was converted. Then, the conversion rate gradually slowed down, and conversion was achieved in 85% yield after 24 h. The above results indicate





Scheme 3 Mechanistic experiments.

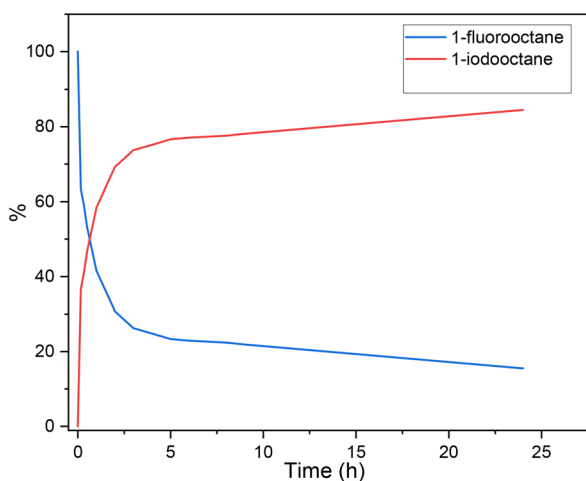


Fig. 1 Kinetic profile of the halogen exchange reaction between 1-fluorooctane and 1-iodooctane.

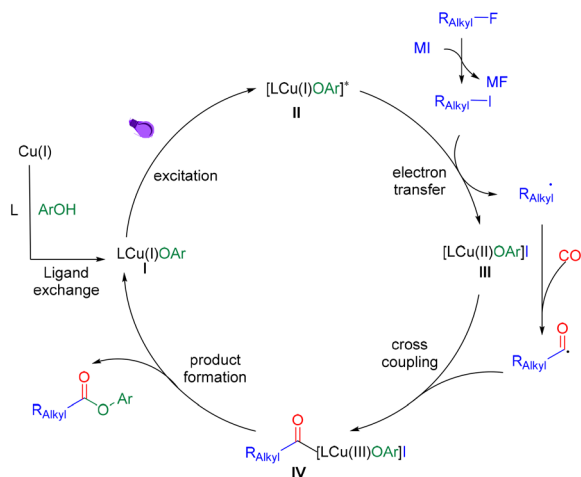
that the rate-determining step of our reaction is not halogen exchange. Subsequently, alkyl iodide was tested in this reaction. The reaction of **1b** at room temperature or under heating all gave the desired product in good yields (Scheme 3a-II), which means heating is not necessary for the proceeding of alkoxy carbonylation. For a better understanding of the role of magnesium iodide in this reaction, reactions with alkyl iodide and metal fluoride were performed under our standard conditions. The results show that magnesium fluoride has no effect on the carbonylation (Scheme 3a-III). However, when using other fluorides as additives, the reaction gave no desired ester product but converted back to alkyl fluoride (Scheme 3a-

IV). More specifically, halogen exchange is a reversible reaction, and in the presence of fluoride ions, alkyl iodide will preferentially undergo halogen exchange to the more stable alkyl fluoride rather than carbonylation. Thanks to the ultra-low solubility of magnesium fluoride in anisole, our standard reaction is essentially free of fluoride ions, which is the key to the successful achievement of the reaction with good yields of the desired ester products.

To further shed light on the mechanism, additional mechanistic experiments were conducted. When stoichiometric radical scavengers, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 1,1-diphenylethene (1,1-DPE), were added to the model reaction of **1a** and **2a** under standard alkoxy carbonylation conditions, the formation of ester **3a** was completely suppressed. The adducts of olefin with alkyl radical **6a** were detected by GC-MS (Scheme 3b). In the radical inhibition experiments, the yields gradually decreased with the gradual addition of 2,6-di-*tert*-butyl 4-methylphenol (BHT, a radical scavenger, 0–2 equiv.) (Scheme 3c). Subsequently, in radical clock experiments, reactions using phenol and (1-fluorohex-5-en-3-yl)benzene as the substrates, the corresponding cyclization product **7** was obtained as the major ester (Scheme 3d). All these results imply the existence of radical intermediates in the reaction.

Based on the above results and literature reports,^{7–14} we proposed a mechanism for this reaction (Scheme 4). Initially, the $\text{LCu}^{\text{I}}\text{OAr}$ species (**I**) was generated from the copper salt through ligand exchange with phenol and the ligand.¹⁶ Then the complex **I** excited to its excited state adduct **II** under irradiation. Meanwhile, the alkyl fluoride undergoes halogen exchange to generate the corresponding alkyl iodide.





Scheme 4 Proposed mechanism.

Afterwards, complex **II** engaged in a single electron transfer reaction with alkyl iodide to form an alkyl radical and complex **III**. The alkyl radical was then captured by carbon monoxide to afford an acyl radical which will react with complex **III** to give acyl copper complex **IV**. Finally, the target ester can be eliminated by reductive elimination and regenerate Cu^{I} species for the next catalytic cycle.

Conclusions

In summary, we have developed a photoinduced copper-catalyzed alkoxy carbonylation of alkyl fluorides with phenols to synthesize various esters. The remarkable scope and functional group tolerance were evidenced by >50 examples and also the late-stage modification of natural product-related substrates. As the first example of the carbonylation of alkyl fluorides, the procedure provides a new pathway for the functionalization of alkyl fluorides.

Author contributions

X.-F. W. conceived and designed the project; P. Y. and Y.-H. Z. conducted the experiments; P.Y. analysed and interpreted the experimental data; P. Y. and X.-F. W. prepared the manuscript; P. Y. and X.-F. W. prepared the ESI.†

Conflicts of interest

There are no conflicts to declare.

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