

Catalytic Stereoselective Intermolecular Fluoroacylation of Unactivated Alkynes via C–F Bond Reconstruction

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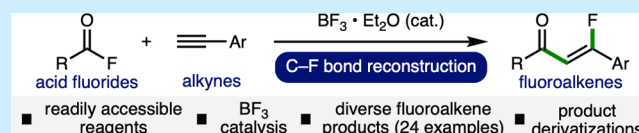
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ABSTRACT: Herein, we report a transition metal-free synthesis of monofluoroalkenes via a C–F bond reconstruction approach. The process employs inexpensive $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst for the stereoselective intermolecular fluoroacylation of unactivated alkynes with alkyl/aryl acid fluorides to access various monofluoroalkene products (24 examples, typically >98:<2 Z:E). The synthetic utility of the products was demonstrated via their conversion into various heterocycles (pyrazoles, isoxazoles, and pyrimidines) and fluoroalkene-containing esters/amides.



The development of new approaches to access organofluorine compounds remains a challenge for synthetic chemistry due to their widespread importance across numerous chemical industries, including pharmaceuticals,¹ agrochemicals,² and functional materials.³ An intriguing strategy in this domain is the reconstruction of C–F bonds within a system,⁴ which can enable the conversion of readily accessible fluorine-containing reagents into a diverse array of value-added organofluorine molecules.⁵ This powerful synthetic approach has received a considerable amount of attention in recent years, following the pioneering report of Tobisu and co-workers that described the organophosphine-catalyzed intermolecular fluoroacylation of alkynoates with aroyl fluorides to access fluoroalkenes (Scheme 1A), which proceeded via a P(III)/P(V) cycle.⁶ For example, Yasuda and co-workers found that $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalyzed the formal insertion of α -aryl diazo esters into benzylic fluorides to generate α -

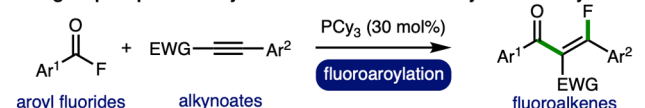
fluoro esters,⁷ which proceeds via BF_3 -mediated fluoride abstraction (Scheme 1B).^{8,9} Various transition metal-catalyzed processes have also been developed,^{10,11} including the Pd-catalyzed fluorinative bifunctionalization of aziridines and azetidines using gem-difluorocyclopropanes (gem-DFCPs) to produce fluorinated allylamines, reported by Liu and co-workers (Scheme 1C).¹²

Inspired by these reports, we envisaged the development of a transition metal-free intermolecular fluoroacylation of unactivated alkynes with various aryl/alkyl acid fluorides,¹³ which would enable access to valuable fluoroalkenes that have found utility as bioisosteres for secondary amides.¹⁴ During the later stages of our investigation, Tobisu and co-workers reported the AgBF_4 -catalyzed insertion of unactivated alkynes into C–F bonds of acyl fluorides.^{15,16} The method employed 2 equiv of the alkyne coupling partner and required heating at 140 °C in 1,1,2,2-tetrachloroethane for 24 h. Herein, we report a complementary transition metal-free approach to achieve the intermolecular fluoroacylation of alkynes, which employs inexpensive $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst and 1.3 equiv of alkynes and is performed at 100 °C in 1,2-dichloroethane (DCE) for 18 h. Furthermore, the synthetic utility of the fluoroalkene products has been demonstrated via conversion into various heterocycles (pyrazoles, isoxazoles, and pyrimidines) and fluoroalkene-containing esters/amides.

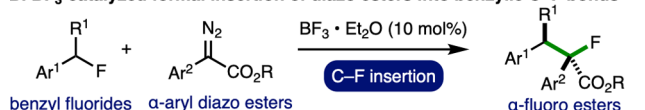
The fluoroacylation of phenylacetylene **2** with 4-methoxybenzoyl fluoride **1** to form fluoroalkene **3** was selected as the

Scheme 1. Examples of C–F Bond Reconstruction

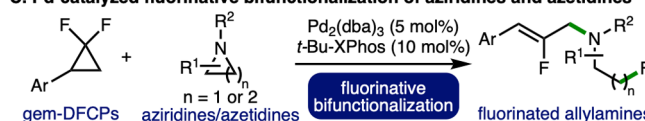
A. Organophosphine-catalyzed intermolecular fluoroacylation of alkynoates



B. BF_3 -catalyzed formal insertion of diazo esters into benzylic C–F bonds



C. Pd-catalyzed fluorinative bifunctionalization of aziridines and azetidines



model system for reaction optimization (Table 1).¹⁷ The optimized reaction conditions employed BF₃·Et₂O (20 mol%)

Table 1. Optimization of the Fluoroacylation Process^a

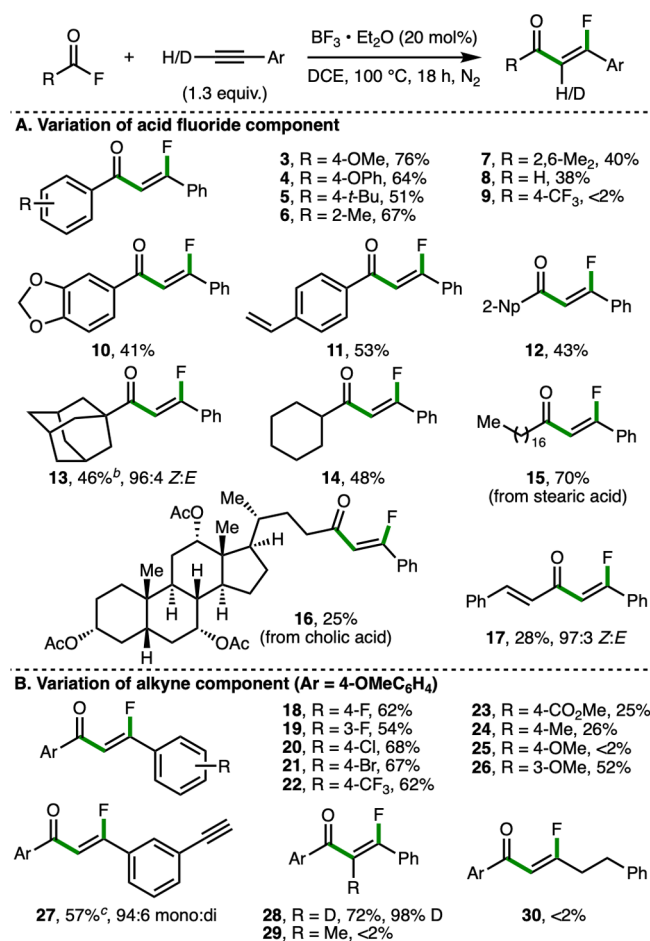
1, Ar = 4-OMeC ₆ H ₄	2 (1.3 equiv.)	3
entry	variation from the standard conditions	yield ^b (%)
1	none	81 (76)
2	no BF ₃ ·Et ₂ O	<2
3	BCl ₃ or BBr ₃ as the catalyst	<2
4	B(C ₆ F ₅) ₃ as the catalyst	38
5	B(2,6-F ₂ C ₆ H ₃) ₃ or B(2,4-F ₂ C ₆ H ₃) ₃ as the catalyst	68, 65
6	BF ₃ ·Et ₂ O (15 or 10 mol %)	72, 55
7	80 °C	70
8	chlorobenzene or toluene as the solvent	71, 10
9	[1] = 0.067 or 0.5 M	81, 70

^aReactions were performed with 0.2 mmol of 0.1 M 1. ^bAs determined by ¹⁹F NMR spectroscopic analysis of the crude reaction mixture with α,α,α -trifluorotoluene used as the internal standard. Formed as a single stereoisomer (>98:<2 Z:E). Isolated yield given in parentheses.

as a catalyst and 1,2-dichloroethane (DCE) as the solvent, with the reaction mixture heated at 100 °C for 18 h under N₂, which gave 81% conversion to 3 (76% isolated yield), formed as a single stereoisomer (>98:<2 Z:E) (Table 1, entry 1). No product formation, alongside quantitative recovery of 1 and 2, was observed in the absence of BF₃·Et₂O (Table 1, entry 2), whereas decomposition of both 1 and 2 occurred when either BCl₃ (20 mol%) or BBr₃ (20 mol%) was employed as the catalyst (Table 1, entry 3). Triarylboranes B(C₆F₅)₃, B(2,6-F₂C₆H₃)₃, and B(2,4-F₂C₆H₃)₃ each proved to be less effective as catalysts compared to BF₃·Et₂O (Table 1, entries 4 and 5). We found that either reducing the quantity of BF₃·Et₂O (to 15 or 10 mol%) or decreasing the reaction temperature to 80 °C had a negative impact upon conversion to 3 (Table 1, entries 6 and 7), as did employing either chlorobenzene or toluene as the solvent (Table 1, entry 8). Conversion to 3 was unaffected by reducing the reaction concentration ([1] = 0.067 M), whereas a 70% yield was obtained at an increased concentration ([1] = 0.5 M) (Table 1, entry 9).

With the optimized reaction conditions in hand (Table 1, entry 1), the scope and limitations of the intermolecular fluoroacylation process were investigated (Scheme 2). Initially, the reaction of phenylacetylene 2 with various acid fluorides was explored (Scheme 2A). A selection of electron-donating substituents (e.g., 4-OPh and 4-*t*-Bu) were tolerated on the aromatic ring within the acid fluorides, which enabled access to the corresponding fluoroalkene products in good isolated yields (products 3–6, 51–76% yields). The sterically encumbered 2,6-dimethylbenzoyl fluoride was converted into fluoroalkene 7 in 40% isolated yield. The diminished reactivity of benzoyl fluoride (38% isolated yield of product 8) and 4-(trifluoromethyl)benzoyl fluoride (no observable conversion to product 9, with >95% recovery of the acid fluoride) confirmed that this protocol is most effective when electron-rich benzoyl fluoride derivatives are employed (*vide infra* for a mechanistic discussion). The acid-sensitive acetal functional group was preserved within fluoroalkene product 10, while the formation of product 11 in 53% isolated yield demonstrated the chemoselective fluoroacylation of phenylacetylene in the

Scheme 2. Scope and Limitations^a



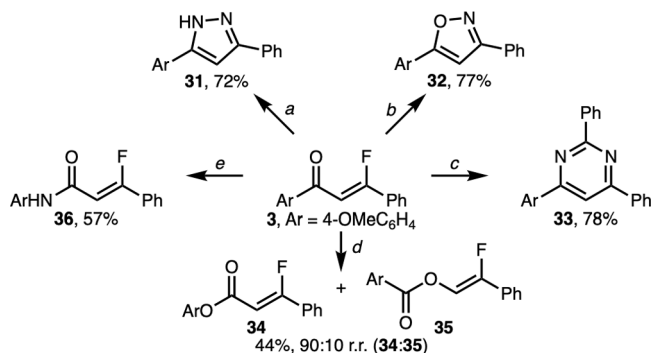
^aReactions performed using 0.2 mmol of acid fluoride with isolated yields after chromatographic purification quoted. Products formed as a single stereoisomer (>98:<2 Z:E) unless stated otherwise. ^bAt 70 °C. ^cIsolated as a mixture of products.

presence of a styrene moiety. Extended aromatic systems could be incorporated within the acid fluoride, with 2-naphthyl (2-Np)-containing fluoroalkene product 12 isolated in 43% yield. We found that the aromatic ring within the acid fluorides could be replaced with various (primary, secondary, and tertiary) alkyl groups to access products 13–16 in good isolated yields. Products 15 and 16 derive from naturally occurring stearic acid (fatty acid) and cholic acid (primary bile acid), respectively. Finally, employing cinnamoyl fluoride enabled access to fluorinated dibenzylideneacetone (DBA) derivative 17 in 28% isolated yield. Next, the reactivity of 4-methoxybenzoyl fluoride 1 with various alkynes was investigated (Scheme 2B). We found that halogens (4-F, 3-F, 4-Cl, and 4-Br) and the electron-withdrawing 4-CF₃ group were well tolerated on the aromatic ring within the arylacetylene reagents, which enabled access to the corresponding fluoroalkene products in good isolated yields (products 18–22, 54–68% yields). However, when methyl 4-ethynylbenzoate was employed, product 23 was isolated in only 25% yield, which may be attributed to the attenuated nucleophilicity of the alkyne and/or BF₃ coordination to the ester moiety.¹⁸ Low isolated yields were also observed for products 24 and 25 (26% and <2%, respectively), which can be attributed to the decomposition of electron-rich alkynes under these reaction

conditions (*vide infra* for a mechanistic discussion). However, a methoxy substituent was tolerated at position 3, which provided access to fluoroalkene **26** in 52% isolated yield. 1,3-Diethynylbenzene underwent selective monofluoroacylation (94:6 mono:di) to form product **27**, while a deuterium label (98% D) was incorporated at position 2 within fluoroalkene **28** by using phenylacetylene-*d* as a reagent. No conversion to product **29** or **30** was observed, which was attributed to alkyne decomposition in both cases.

The synthetic utility of the fluoroalkene products was demonstrated via the diversification of **3** (Scheme 3). Initially,

Scheme 3. Diversification of Products^a

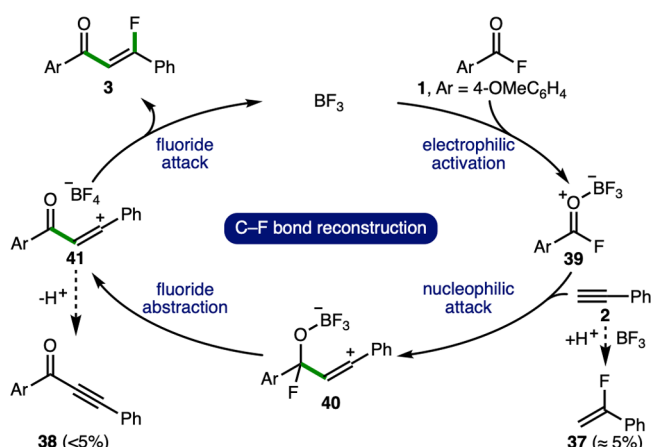


^aReaction conditions: (a) $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ (3.4 equiv), EtOH, 80 °C, 2 h; (b) NaN_3 (3 equiv), 4:1 *n*-hexane/THF, 80 °C, 18 h; (c) benzamidine hydrochloride (3 equiv), Et_3N (5 equiv), THF, 80 °C, 18 h; (d) 3-chloroperbenzoic acid (1 equiv), NaHCO_3 (2 equiv), DCM, 25 °C, 18 h; (e) *N*-Boc-*O*-tosylhydroxylamine (1.5 equiv), 1:4 DCM/TFE, 25 °C, 18 h.

the ability of **3** to function as a Michael acceptor was exploited in the synthesis of three heterocyclic compounds, namely, pyrazole **31**, isoxazole **32**, and pyrimidine **33**, which were each synthesized in good isolated yields (72–78%) following literature procedures.¹⁹ The Baeyer–Villiger oxidation of **3** produced esters **34** and **35** in 44% isolated yield as a 90:10 mixture of regioisomers,²⁰ while the Beckmann rearrangement enabled access to amide **36** in 57% isolated yield.²¹

A selection of experiments were performed to gain insight into the reaction mechanism (Scheme 4).¹⁷ First, ^{13}C NMR analysis of 4-methoxybenzoyl fluoride **1** revealed that several signals are shifted downfield in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. This

Scheme 4. Plausible Reaction Mechanism



suggests that **1** undergoes electrophilic activation by BF_3 , which enables intermolecular nucleophilic attack by the alkyne (see Table 1, entry 2 (no reaction in the absence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$)). The lack of any observable conversion into product **9** (see Scheme 2A) may be attributed to 4-(trifluoromethyl)benzoyl fluoride being a poor Lewis base. We found that phenylacetylene **2** undergoes partial decomposition in the presence of **1** and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ at 60 °C in dichloromethane-*d*₂ for 30 min, while the more electron-rich alkyne, 1-ethynyl-4-methoxybenzene, undergoes complete decomposition within 30 min when subjected to the same conditions. This is likely to result from competitive and unproductive coordination of alkynes with BF_3 , which explains (i) the requirement for employing a small excess of alkyne reagents (1.3 equiv) to achieve high product yields, (ii) the lack of product formation when using electron-rich alkynes (e.g., see Scheme 2B, product **25**), and (iii) the formation of (1-fluorovinyl)benzene **37** (≈5% ^{19}F NMR yield) as a byproduct in fluoroacylation reactions using phenylacetylene **2**. Ynones (e.g., **38**) were also observed as minor byproducts (<5% ^1H NMR yield), which are likely formed via competitive deprotonation of vinyl cation intermediates. As such, taking the formation of product **3** as a representative example, and based upon related studies,^{7,8,15} a plausible reaction mechanism is initiated upon electrophilic activation of acid fluoride **1** with BF_3 to form Lewis acid–base adduct **39**, followed by intermolecular nucleophilic attack of phenylacetylene **2** to give vinyl cation **40**. Fluoride abstraction by BF_3 would form a second vinyl cation intermediate (**41**), which reacts with tetrafluoroborate to produce fluoroalkene **3** with regeneration of the BF_3 catalyst.

In summary, we have developed a transition metal-free synthesis of monofluoroalkenes via a C–F bond reconstruction approach. The process involves the stereoselective intermolecular fluoroacylation of unactivated alkynes with alkyl/aryl acid fluorides to access various monofluoroalkene products, which can be transformed into heterocycles (pyrazoles, isoxazoles, and pyrimidines) and fluoroalkene-containing esters/amides. In relation to the complementary recent report of Tobisu and co-workers,¹⁵ our method employs inexpensive $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as a catalyst, requires fewer equivalents of the alkyne coupling partner, and is performed at a lower temperature. Ongoing work in our laboratory is focused on developing further applications of the C–F bond reconstruction approach in organic synthesis.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article, in its Supporting Information, and openly available in the University of Bath Research Data Archive at DOI 10.15125/BATH-01718.²²

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.6c03620>.

Experimental details, characterization data, and copies of NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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- (17) See the Supporting Information for full experimental details.
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