Organic LETTERS

Letter

Cite This: Org. Lett. XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Copper-Catalyzed Fluoroolefination of Silyl Enol Ethers and Ketones toward the Synthesis of β-Fluoroenones

Yanlin Li,[†] Jing Liu,[†] Shuang Zhao,[†] Xuzhao Du,[†] Minjie Guo,*[,‡] Wentao Zhao,[†] Xiangyang Tang,[†] and Guangwei Wang*[,†]

[†]Tianjin Key Laboratory of Molecular Optoelectronic Science, Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, P. R. China

[‡]Institute for Molecular Design and Synthesis, Health and Science Platform, Tianjin University, Tianjin 300072, P. R. China

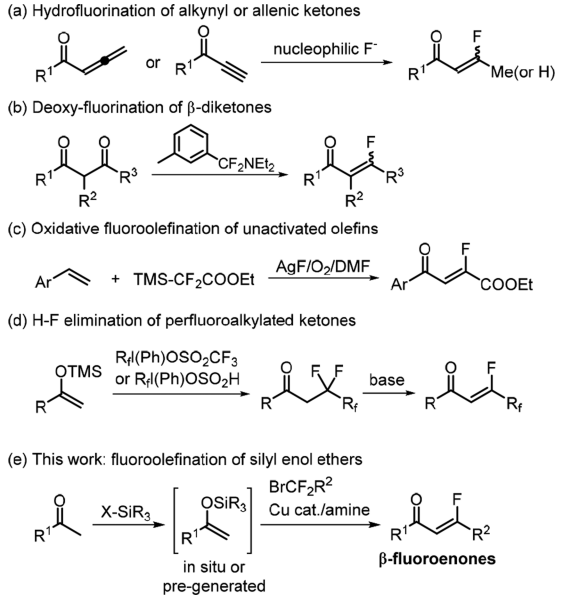
Supporting Information

ABSTRACT: A general and facile synthetic method for β-fluoroenones from silyl enol ethers or ketones, with a copper−amine catalyst system, has been developed. The reaction proceeded by a tandem process of difluoroalkylation−hydrolysis−dehydrofluorination. This method is characterized by high yields, excellent *Z*/*E* ratios, a low-cost catalyst, and a broad substrate scope. The synthetic potential of β-fluoroenones has been demonstrated by the construction of various complicated organofluorine molecules.

Development of practical strategies for the introduction of fluorine and fluorine-containing functional groups is the major issue in organofluorine chemistry.[1] In particular, the synthesis of monofluoroolefins has been the focus of interest since the resulting products provide important building blocks and enormous potential of synthesis for various complex organofluorine compounds.[2]

Recently, we have developed a copper−amine catalyzed difluoro-/perfluoroalkylation of general alkenes and heteroarenes.[3] In this context, we chose silyl enol ethers which contain electron-rich alkene moieties as the substrate for difluoro-/perfluoroalkylation. We propose that the expected product might undergo hydrolysis to afford α-difluoro-/perfluoroalkylated ketones due to the instability of silyl enol ethers. However, instead of a difluoroalkylated ketone and difluoroalkylated enolate, β-fluoroenones were obtained utilizing a copper−amine catalyst system. To date, although the synthesis of α-fluoroenones had been exploited successfully,[4] the methods for the synthesis of β-fluoroenones are rather limited. For example, hydrofluorination of alkynyl or allenic ketones[5] (Scheme 1a) and deoxyfluorination of β-diketones led to *Z*/*E* isomeric mixtures of β-fluoroenones[6] (Scheme 1b). Oxidative fluoroolefination has also been developed for the construction β-fluoroenones from alkenes and ethyl trimethylsilyl difluoroacetic ester[7] (Scheme 1c). In addition, perfluoroalkylation of silyl enolates using cationic perfluoroalkylating agents followed by base-mediated dehydrofluorination of perfluoroalkylated ketones has also been reported to afford perfluoroalkyl substituted β-fluoroenone[8] (Scheme 1d). Therefore, the synthesis of β-fluoroenone from easily available starting materials and cheap catalysts are still underdeveloped. Inspired by our promising results, we aimed at optimizing the conditions to establish a convenient strategy for the synthesis of β-fluoroenone from ketones or enolate with ethyl bromodifluoroacetate, which has received considerable interest as an inexpensive and commercially available difluoroalkyl source.[9−13] The expected β-fluoroenones are amenable to various transforamtions due to their multifunctionality.

Scheme 1. Synthetic Routes to β-Fluoroenones



Initially, the reaction of trimethylsilyl enol ether with 1.5 equiv of ethyl bromodifluoroacetate (**2a**) was performed in the presence of 10 mol % of CuI and 1.5 equiv of PMDETA (pentamethyldiethylenetriamine) in acetonitrile (0.2 M) at 80 °C under an inert atmosphere. Instead of forming the routine

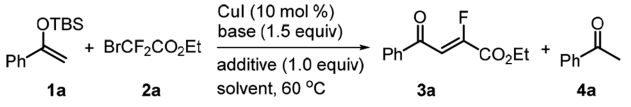
Received: November 29, 2017

DOI: 10.1021/acs.orglett.7b03700
Org. Lett. XXXX, XXX, XXX−XXX

difluoroalkylated product, an unexpected product of β-fluoroenones (**3a**) was afforded in a low yield (13%), accompanied by the hydrolyzed byproduct acetophenone (**4a**) (54%) (Table 1, entry 1). The formation of β-fluoroenones can be derived from the Heck-type reaction−hydrolysis−dehydrofluorination[14] cascade reaction process of silyl enol ethers. The poor stability of trimethylsilyl enol ether may be responsible for the low yielding. To our delight, employment of more stable *tert*-butyldimethylsilyl (TBS) enol ether improved the yield of target product **3a** to 79% (Z/E = 12/1) with the yield of **4a** decreasing to 17% (Table 1, entry 2). In order to completely inhibit the hydrolysis of silyl enol ethers, the trimethylsilyl chloride (TMSCl) was utilized to trap the trace amount of moisture (Table 1, entry 3) and a 90% (Z/E = 22/1) yield of **3a** was obtained under these conditions. Then, different kinds of silyl chlorides were examined (Table 1, entries 4−6), and the results indicated TMSCl, TESCl, TBSCl afforded similar yields with acceptable Z/E ratios. Considering the relative stability and appropriate boiling point of TESCl, we chose TESCl as the optimal additive. Several other solvents had been tried (Table 1, entries 7−10), and lower yields resulted. It is noteworthy that PMDETA played a crucial role in this reaction, as replacement with other ligands led to lower yields (Table 1, entries 11−14). The superior results of PMDETA should be attributed to its excellent capacity to facilitate the generation and stabilization of related radicals by coordination with the copper atom.[15] Meanwhile, various cuprous salt catalysts were investigated, which revealed that three different kinds of cuprous salt catalysts led to similar yields with different Z/E ratios. The relatively stable CuI was chosen as the optimal catalyst (Table 1, entries 15 and 16). When the dosage of PMDETA decreased to 0.5 equiv, the yield of target product dropped slightly with a distinct decrease of Z/E ratio (Table 1, entry 17). When the amount of TESCl was decreased to 0.5 equiv, a slightly lower yield (85%) and lower Z/E ratio (13/1) were obtained (Table 1, entry 18). When the amount of CuI was decreased to 1 mol %, the yield of the target product dropped to 6% together with 7% of acetophenone and ∼70% of starting material (**1a**) being recovered.

With the optimized reaction conditions in hand (Table 1, entry 4), the substrate scope of silyl enol ethers has been explored (Scheme 2). First, the substitutions on aromatic rings have been studied. Both electron-donating groups and weak electron-withdrawing groups (**3a**−**3j**, **3l**−**3o**, **3u**) can lead to satisfactory results, while strong electron-withdrawing groups (**3k**) led to a moderate yield. Silyl enol ethers derived from heteroaromatic ketones also gave good yields (**3p**−**3t**). Compared with **3q** and **3r**, **3p** displayed a higher yield, which might be due to their different coordination patterns. Cyclohexanone and cyclopentanone derived silyl enol ether also led to desired products (**3u**, **3v**) in moderate to good yields. Another aliphatic silyl enol ether was also examined, and **3w** was achieved with a moderate yield and remarkable Z/E ratio. Considering the possible Z/E isomerization of activated olefins under light,[16] parallel experiments for **3j** as a model test have been conducted under light and dark conditions, and similar results were obtained (see Supporting Information (SI)).

Table 1. Optimization of Reaction Conditions[a]

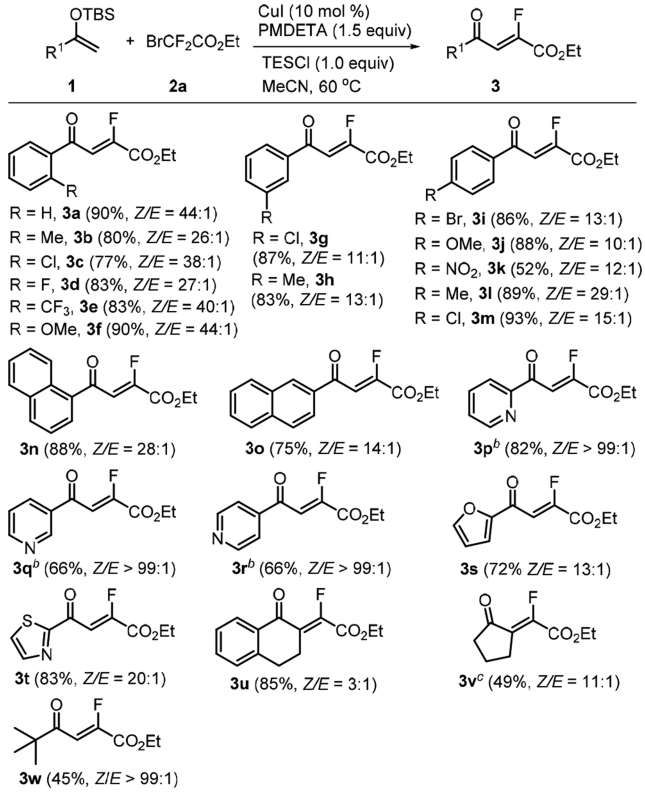


1a 2a 3a 4a

entry	base	additive	sol.	**3a** (%)[b] (Z/E)	**4a**[b] (%)
1[c]	PMDETA	none	MeCNN	13 (12:1)	54
2	PMDETA	none	MeCN	79 (12:1)	17
3	PMDETA	TMSCl	MeCN	90 (22:1)	<1
4	PMDETA	TESCl	MeCN	90 (44:1)	<1
5	PMDETA	TBSCl	MeCN	86 (14:1)	5
6	PMDETA	TBSOTf	MeCN	51 (12:1)	<1
7	PMDETA	TESCl	THF	65 (12:1)	<1
8	PMDETA	TESCl	toluene	7	<1
9	PMDETA	TESCl	dioxane	69 (13:1)	<1
10	PMDETA	TESCl	DMF	82 (11:1)	<1
11	TMEDA	TESCl	MeCN	<5	29
12	TMPDA	TESCl	MeCN	5	34
13	NEt_3	TESCl	MeCN	<1	74
14	pyridine	TESCl	MeCN	<1	71
15[d]	PMDETA	TESCl	MeCN	88 (21:1)	<1
16[e]	PMDETA	TESCl	MeCN	86 (13:1)	5
17[f]	PMDETA	TESCl	MeCN	86 (4:1)	<1
18[g]	PMDETA	TESCl	MeCN	85 (13:1)	<1

[a]Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (1.0 mmol), **2a** (1.5 mmol), base (1.5 mmol), and CuI (10 mol %), in solvent (2 mL) at 60 °C under Ar for 12 h. [b]Detected by GC. [c]Trimethylsilyl enol ether as reactant at 80 °C. [d]CuCl instead of CuI. [e]CuBr instead of CuI. [f]0.5 equiv of PMDETA was added. [g]0.5 equiv of TESCl was added.

Scheme 2. Copper-Catalyzed Fluoroolefination of Silyl Enol Ethers with Ethyl Bromodifluoroacetate[a]



1 2a 3

R = H, **3a** (90%, Z/E = 44:1)
R = Me, **3b** (80%, Z/E = 26:1)
R = Cl, **3c** (77%, Z/E = 38:1)
R = F, **3d** (83%, Z/E = 27:1)
R = CF_3, **3e** (83%, Z/E = 40:1)
R = OMe, **3f** (90%, Z/E = 44:1)

R = Cl, **3g** (87%, Z/E = 11:1)
R = Me, **3h** (83%, Z/E = 13:1)

R = Br, **3i** (86%, Z/E = 13:1)
R = OMe, **3j** (88%, Z/E = 10:1)
R = NO_2, **3k** (52%, Z/E = 12:1)
R = Me, **3l** (89%, Z/E = 29:1)
R = Cl, **3m** (93%, Z/E = 15:1)

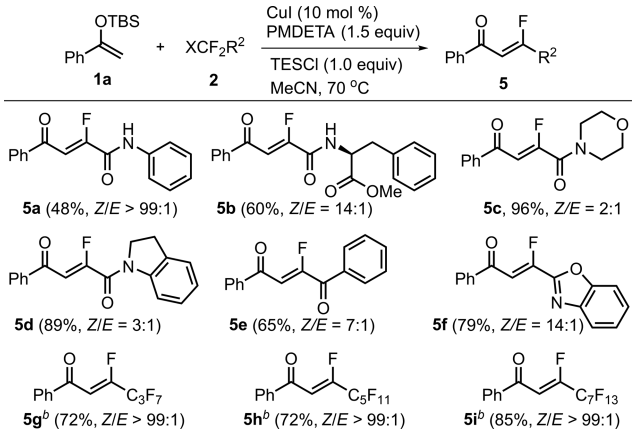
3n (88%, Z/E = 28:1)
3o (75%, Z/E = 14:1)
3p[b] (82%, Z/E > 99:1)
3q[b] (66%, Z/E > 99:1)
3r[b] (66%, Z/E > 99:1)
3s (72% Z/E = 13:1)
3t (83%, Z/E = 20:1)
3u (85%, Z/E = 3:1)
3v[c] (49%, Z/E = 11:1)
3w (45%, Z/E > 99:1)

[a]Reaction conditions: a mixture of silyl enol ethers (**1**) (1.0 mmol), ethyl bromodifluoroacetate (**2a**) (1.5 mmol), CuI (0.1 mmol), PMDETA (1.5 mmol), TESCl (1.0 mmol) in dry MeCN (2.0 mL) was stirred at 60 °C for 14 h. [b]3.0 equiv of ethyl bromodifluoroacetate (**2a**) was used at 80 °C for 2 h. [c]TBSOTf was used instead of TESCl.

DOI: 10.1021/acs.orglett.7b03700
Org. Lett. XXXX, XXX, XXX−XXX

Furthermore, the scope of *gem*-difluoromethylene and perfluoroalkyl compounds was examined (Scheme 3). First, the

Scheme 3. Scope of *gem*-Difluoromethylene/Perfluoroalkyl Compounds[a]

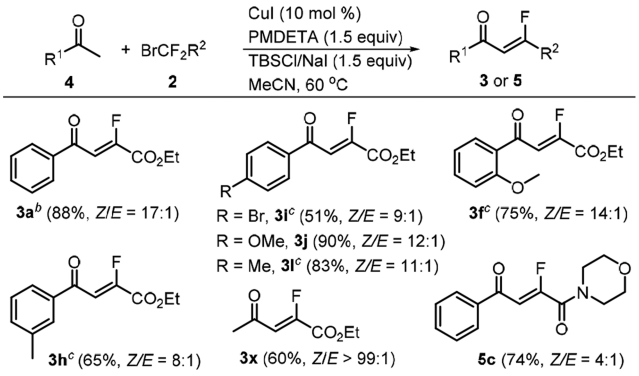


[a]Reaction conditions: a mixture of silyl enol ethers (**1a**) (1.0 mmol), **2** (1.5 mmol), CuI (0.1 mmol), PMDETA (1.5 mmol), TESCl (1.0 mmol) in dry MeCN (2.0 mL) was stirred at 70 °C for 14 h. [b]At 80 °C for 4–6 h.

different kinds of *gem*-difluoromethylene compounds, such as difluoroacetamides, difluoroacetophenone, and 2-(bromodifluoromethyl)benzo[*d*]oxazole, proved to be suitable substrates, resulting in good yields with moderate to excellent *Z*/*E* selectivities (**5a**–**5f**). Moreover, the perfluoroalkyl substrates achieved satisfactory yields with excellent stereoselectivities (**5g**–**5i**).

By comparing the preparation conditions (see SI) of silyl enol ethers with the optimized *β*-fluoroolefination conditions, the one-pot method was designed which involved the *in situ* generation of silyl enol ethers. Starting from acetophenone (**4a**), the reaction proceeded smoothly in the presence of NaI, TBSCl, PMDETA, and CuI (Scheme 4). However, in the absence of NaI, the yield dropped to 5% dramatically with other conditions unchanged. When TMSI, which might promote the enolization of ketone to form silyl enol ethers, was applied, similar results were obtained.

Scheme 4. Examples of One-Pot Method[a]

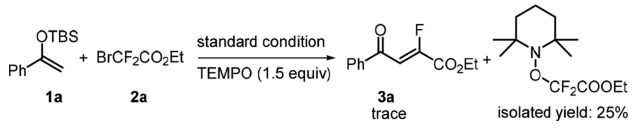


[a]Reaction conditions: a mixture of ketones (**4**) (1.0 mmol), **2** (2.5 mmol), CuI (0.1 mmol), PMDETA (1.5 mmol), TBSCl (1.5 mmol), NaI (1.5 mmol) in dry MeCN (3.0 mL) was stirred at 60 °C for 14 h. [b]10 mmol scale experiment. [c]TMSI (1.5 mmol) was used instead of TBSCl/NaI.

Both electron-donating and -withdrawing groups at different locations of the benzene ring could be well tolerated, with the electron-donating groups leading to higher yields while electron-withdrawing groups led to slightly lower yields (Scheme 4). Importantly, a multigram-scale experiment had been conducted with **4a** and **2a** as starting material, and **3a** was obtained in satisfactory yield.

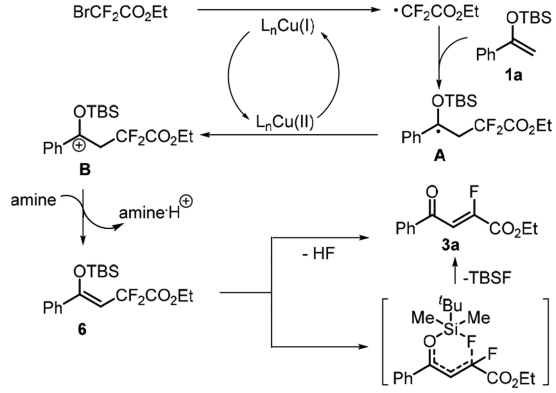
To gain some insight into the mechanism, 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO) as a radical scavenger was added to this reaction. The reaction was completely inhibited with TEMPO–CF_2CO_2Et being isolated as the major product (Scheme 5). On the basis of the above-mentioned results and

Scheme 5. TEMPO Experiment



relevant literature,[3,14] a possible reaction mechanism was proposed as illustrated in Scheme 6. Initially, oxidation of

Scheme 6. Possible Mechanism



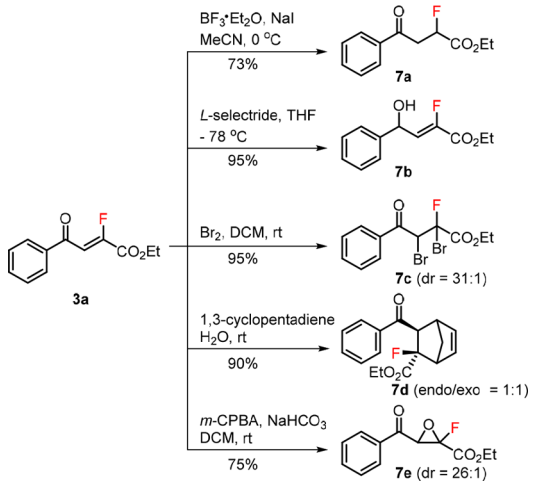
copper(I) species by a fluoroalkyl reagent through a single electron transfer (SET) process results in a copper(II) species and fluoroalkyl radical. Then, addition of the fluoroalkyl radical to silyl enol ether generates radical species **A** which can be oxidized by the copper(II) species to afford carbocation species **B** and regenerate the copper(I) species. *β*-H Elimination of **B** leads to fluoroalkylated silyl enol ether **6** which might undergo the hydrolysis–dehydrofluorination process or direct defluorosilylation reaction through a possible six-membered ring transition state, either of which leading to a *β*-fluoroenone product.

With the optimized reaction conditions in hand, further derivatization of *β*-fluoroenones was explored. A variety of reaction types had been accomplished, such as selective reduction of a carbonyl or olefin bond, olefin addition, Diels–Alder reaction, and epoxidation reaction (Scheme 7). A series of *β*-fluorinated carbonyl derivatives had been obtained with good to excellent yields, which indicate the diverse potential of *β*-fluoroenones as key synthetic intermediates for construction of various fluorine-containing compounds.

In summary, the Cu-catalyzed reaction of ethyl bromodifluoroacetate and silyl enol ethers has been developed, which provides a facile strategy toward the synthesis of *β*-fluoroenones. Various substitutions on the phenyl ring of acetophones can be well tolerated. Perfluoroalkyl iodides and various bromodifluoro-

DOI: 10.1021/acs.orglett.7b03700
Org. Lett. XXXX, XXX, XXX–XXX

Scheme 7. Further Derivatization of β-Fluoroenones



acetamide also serve as suitable substrates for this catalyst system. Moreover, the one-pot strategy has been achieved which involved *in situ* generation of silyl enol ethers directly from ketones. The resulting β-fluoroenones have been successfully functionalized through diverse types of reactions. A preliminary mechanistic study indicated that a radical pathway was involved in this transformation. Further studies to elucidate the mechanism and exploit possible synthetic applications are underway in our group.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b03700.

Experimental procedures, spectral and analytical data, copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: wanggw@tju.edu.cn.
*E-mail: gmj2016@tju.edu.cn.

ORCID

Guangwei Wang: 0000-0003-4466-9809

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Basic Research Program of China (No. 2015CB856500), the Natural Science Foundation of Tianjin (No. 16JCYBJC20100), and Tianjin City Thousand Talents Program for support of this research.

■ REFERENCES

(1) (a) *Biomedicinal Aspects of Fluorine Chemistry*; Filler, R., Kobayashi, Y., Eds.; Elsevier: Amsterdam, 1982. (b) *Fluorine in Bioorganic Chemistry*; Welch, J. T., Eswarakrishman, S., Eds.; Wiley-Interscience: New York, 1991. (c) Champagne, P. A.; Desroches, J.; Hamel, J.-D.; Vandamme, M.; Paquin, J.-F. *Chem. Rev.* **2015**, *115*, 9073. (d) Xu, T.; Mu, X.; Peng, H.; Liu, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 8176.

(2) (a) Champagne, P. A.; Desroches, J.; Hamel, J.-D.; Vandamme, M.; Paquin, J.-F. *Chem. Rev.* **2015**, *115*, 9073. (b) Dutheuil, G.; Couve-Bonnaire, S.; Pannecoucke, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 1290. (c) Nakamura, Y.; Okada, M.; Koura, M.; Tojo, M.; Saito, A.; Sato, A.; Taguchi, T. *J. Fluorine Chem.* **2006**, *127*, 627. (d) Okada, M.; Nakamura, Y.; Saito, A.; Sato, A.; Horikawa, H.; Taguchi, T. *Tetrahedron Lett.* **2002**, *43*, 5845. (e) Nakamura, Y.; Okada, M.; Sato, A.; Horikawa, H.; Koura, M.; Saito, A.; Taguchi, T. *Tetrahedron* **2005**, *61*, 5741.

(3) (a) Nishikata, T.; Noda, Y.; Fujimoto, R.; Sakashita, T. *J. Am. Chem. Soc.* **2013**, *135*, 16372. (b) Noda, Y.; Nishikata, T. *Chem. Commun.* **2017**, *53*, 5017. (c) Chen, X.; Liu, X.; Mohr, J. T. *J. Am. Chem. Soc.* **2016**, *138*, 6364. (d) Wang, X.; Zhao, S.; Liu, J.; Zhu, D.; Guo, M.; Tang, X.; Wang, G. *Org. Lett.* **2017**, *19*, 4187. (e) Chen, H.; Wang, X.; Guo, M.; Zhao, W.; Tang, X.; Wang, G. *Org. Chem. Front.* **2017**, *4*, 2403.

(4) (a) Dutheuil, G.; Couve-Bonnaire, S.; Pannecoucke, X. *Angew. Chem., Int. Ed.* **2007**, *46*, 1290. (b) de Haro, T.; Nevado, C. *Chem. Commun.* **2011**, *47*, 248. (c) Ghosh, A. K.; Banerjee, S.; Sinha, S.; Kang, S. B.; Zajc, B. *J. Org. Chem.* **2009**, *74*, 3689. (d) Dutheuil, G.; Paturel, C.; Lei, X.; Couve-Bonnaire, S.; Pannecoucke, X. *J. Org. Chem.* **2006**, *71*, 4316. (e) Ramb, D. C.; Lerchen, A.; Kischkewitz, M.; Beutel, B.; Fustero, S.; Haufe, G. *Eur. J. Org. Chem.* **2016**, *2016*, 1751. (f) Chen, C.; Wilcoxen, K.; Huang, C. Q.; Strack, N.; McCarthy, J. R. *J. Fluorine Chem.* **2000**, *101*, 285. (g) He, Y.; Zhang, X.; Shen, N.; Fan, X. *J. Fluorine Chem.* **2013**, *156*, 9. (h) Chen, C.; Wilcoxen, K.; Zhu, Y.-F.; Kim, K.; McCarthy, J. R. *J. Org. Chem.* **1999**, *64*, 3476. (i) Song, X.; Chang, J.; Zhu, D.; Li, J.; Xu, C.; Liu, Q.; Wang, M. *Org. Lett.* **2015**, *17*, 1712. (j) Xu, J.; Burton, D. J. *J. Org. Chem.* **2005**, *70*, 4346. (k) Hata, H.; Kobayashi, T.; Amii, H.; Uneyama, K.; Welch, J. T. *Tetrahedron Lett.* **2002**, *43*, 6099. (l) Bainbridge, J. M.; Corr, S.; Kanai, M.; Percy, J. M. *Tetrahedron Lett.* **2000**, *41*, 971. (m) Dutheuil, G.; Couve-Bonnaire, S.; Pannecoucke, X. *Tetrahedron* **2009**, *65*, 6034. (n) Hopkinson, M. N.; Giuffredi, G. T.; Gee, A. D.; Gouverneur, V. *Synlett* **2010**, *2010*, 2737.

(5) (a) Li, Y.; Liu, X.; Ma, D.; Liu, B.; Jiang, H. *Adv. Synth. Catal.* **2012**, *354*, 2683. (b) Albert, P.; Cousseau, J. *J. Chem. Soc., Chem. Commun.* **1985**, 961. (c) He, Y.; Shen, N.; Fan, X.; Zhang, X. *Tetrahedron* **2013**, *69*, 8818.

(6) Sano, K.; Fukuhara, T.; Hara, S. *J. Fluorine Chem.* **2009**, *130*, 708.

(7) Liu, C.; Shi, E.; Xu, F.; Luo, Q.; Wang, H.; Chen, J.; Wan, X. *Chem. Commun.* **2015**, *51*, 1214.

(8) Umemoto, T.; Kuriu, Y.; Nakayama, S.; Miyano, O. *Tetrahedron Lett.* **1982**, *23*, 1471.

(9) Besset, T.; Poisson, T.; Pannecoucke, X. *Eur. J. Org. Chem.* **2014**, *2014*, 7220.

(10) (a) Xiao, Y.-L.; Guo, W.-H.; He, G.-Z.; Pan, Q.; Zhang, X. *Angew. Chem., Int. Ed.* **2014**, *53*, 9909. (b) Feng, Z.; Min, Q.-Q.; Zhang, X. *Org. Lett.* **2016**, *18*, 44. (c) Qi, Q.; Shen, Q.; Lu, L. *J. Am. Chem. Soc.* **2012**, *134*, 6548.

(11) (a) Belhomme, M.-C.; Poisson, T.; Pannecoucke, X. *J. Org. Chem.* **2014**, *79*, 7205. (b) Lin, Q.; Chu, L.; Qing, F.-L. *Chin. J. Chem.* **2013**, *31*, 885. (c) Shao, C.; Shi, G.; Zhang, Y.; Pan, S.; Guan, X. *Org. Lett.* **2015**, *17*, 2652. (d) Belhomme, M.-C.; Bayle, A.; Poisson, T.; Pannecoucke, X. *Eur. J. Org. Chem.* **2015**, *2015*, 1719.

(12) Ye, Z.; Gettys, K. E.; Shen, X.; Dai, M. *Org. Lett.* **2015**, *17*, 6074.

(13) (a) Belhomme, M.-C.; Dru, D.; Xiong, H.-Y.; Cahard, D.; Besset, T.; Poisson, T.; Pannecoucke, X. *Synthesis* **2014**, *46*, 1859. (b) Caillot, G.; Dufour, J.; Belhomme, M.-C.; Poisson, T.; Grimaud, L.; Pannecoucke, X.; Gillaizeau, I. *Chem. Commun.* **2014**, *50*, 5887. (c) Belhomme, M.-C.; Poisson, T.; Pannecoucke, X. *Org. Lett.* **2013**, *15*, 3428. (d) Feng, Z.; Min, Q.-Q.; Zhao, H.-Y.; Gu, J.-W.; Zhang, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 1270. (e) Yu, C.; Iqbal, N.; Park, S.; Cho, E. J. *Chem. Commun.* **2014**, *50*, 12884. (f) Li, G.; Wang, T.; Fei, F.; Su, Y.-M.; Li, Y.; Lan, Q.; Wang, X.-S. *Angew. Chem., Int. Ed.* **2016**, *55*, 3491. (g) Xu, P.; Wang, G.; Zhu, Y.; Li, W.; Cheng, Y.; Li, S.; Zhu, C. *Angew. Chem., Int. Ed.* **2016**, *55*, 2939. (h) Chen, Q.; Wang, C.; Zhou, J.; Wang, Y.; Xu, Z.; Wang, R. *J. Org. Chem.* **2016**, *81*, 2639.

(14) (a) Itoh, Y.; Mikami, K. *Org. Lett.* **2005**, *7*, 649. (b) Liu, C.; Shi, E.; Xu, F.; Luo, Q.; Wang, H.; Chen, J.; Wan, X. *Chem. Commun.* **2015**, *51*, 1214.

(15) Eckenhoff, W. T.; Pintauer, T. *Dalton Trans.* **2011**, *40*, 4909.

(16) Metternich, J. B.; Gilmour, R. *J. Am. Chem. Soc.* **2015**, *137*, 11254.

DOI: 10.1021/acs.orglett.7b03700
Org. Lett. XXXX, XXX, XXX−XXX