



Visible-Light-Induced Meerwein Fluoroarylation of Styrenes

Hai-Jun Tang, Bin Zhang, Fei Xue, and Chao Feng*



substituted carbon centers was developed. The protocol features straightforward operation, proceeds under metal-free condition, and accommodates a large variety of synthetically useful functionalities. The critical aspect to the success of this novel transformation lies in using aryldiazonium salts as both aryl radical progenitor and also as single electron acceptor which elegantly enables a radical-polar crossover manifold.



rganofluorine compounds have been finding increasing application in multidiscipline research spanning agrochemical development, pharmaceutical industry, and material sciences, mainly due to their unique physicochemical properties.¹ As such, much effort from synthetic chemists has been directed to elaborating molecular structures of interest by developing site-specific fluorination-based synthetic transformations.² Under this circumstance, transition-metal-catalyzed carbofluorination of π -systems, which not only enables a straightforward incorporation of fluorine atom but also provides an extra opportunity for concurrent integration of carbon-based functionalities such as alkyl,³ trifluoromethyl,⁴ alkynyl,⁵ aryl,⁶ alkoxycarbonyl,⁷ and cyano,⁸ proves to be highly appealing and draws much attention from the synthetic community in recent years. Nonetheless, the progress of fluoroarylation reaction lags far more behind as compared with its counterparts. In this respect, seminal contributions from the groups of Toste,^{6c} Doyle,^{6b} and Gouverneur^{6a} among others have virtually enriched this type of transfroamtion (Scheme 1a). In 2016, we coined a strategy of "F-nucleophilic addition induced functionalization of gem-difluoroalkenes",9 which also finds applications in our recent progress in the arena of fluoroarylation.¹⁰ Furthermore, by resorting to visible-lightpromoted gold redox catalysis, we also successfully extended the fluoroarylation senario to allenoates,¹¹ whereas simple alkene substrates still proved intractable (Scheme 1b). Notwithstanding the advancement in this field, the continuing development of efficacious protocols in this direction is still highly desirable, especially for those that make use of readily available nucleophilic fluorination reagents or accommodate reaction substrates unattainable for prior art.

Since the seminal disclosure of copper-catalyzed aryldiazonium engaged arylation of alkenes by Meerwein in 1939,¹² many advancements of this type arylation have been achieved, which comprise a fertile reaction arsenal for diversity-orientedsyntheses.^{13–16} These reactions proceed via in situ formation Scheme 1. Intermolecular Fluoroarylation of Unsaturated π -Systems

a) Fluoroarylation of alkenes with electrophilic F* reagents (by Toste)



b) Gold-catalyzed fluoroarylation of allenoates using F reagents (Our previous work)



of aryl radical intermediates using progenitors such as aryl halides,¹⁷ arylhydrazines,^{15a} aryldiazonium salts,^{14b,c,15b} or diaryliodonium salts,^{14a} and after radical addition of alkenes three plausible scenarios, including radical coupling and radical-polar crossover through either single-electron reduction or oxidation, may follow. While much progress has been

Received: April 14, 2021 **Published:** May 5, 2021



Organic Letters

achieved for Meerwein carboamination¹⁴ and carbooxygenation,¹⁵ the development of Meerwein-type fluoroarylation is comparatively underdeveloped. In 2012, the Tang group disclosed a silver-catalyzed intermolecular/intramolecular fluoroarylation of styrenes using the expensive Selectfluor as the fluorination reagent,^{6d} despite the fact that the assembly of fluorine-containing fully substituted carbon centers still remains challenging.¹⁸ Later on, Heinrich group reported an intermolecular fluoroarylation of monosubstituted simple alkenes without recourse to metal catalyst, albeit with somewhat depressed reaction efficiency.^{6d} In view of the state of the art in this territory, further development of efficient and practical protocols, particularly those that are amenable for expedient construction of fluorine-containing fully substituted carbon centers, are highly appealing.

Based on the precedents and our own works, we aimed to develop a practical protocol for alkenes fluoroarylation by virtue of the radical-polar crossover manifold using aryldiazonium salt and nucleophilic fluoride as both aryl and fluoro donors (Scheme 1c). The intrinsic property of aryldiazonium salt, which could readily produce aryl radical for reaction initiation under certain conditions^{14b,15c} while also act as single-electron acceptor for efficient reaction propagation was rationalized to lay solid foundation for the feasibility of the proposal. With our long-standing interest in photoredox catalysis and fluorine chemistry,¹⁹ we would like to describe herein a visible-light-induced Meerwein fluoroarylation of styrene derivatives. Notable features with regard to the present protocol include the followings: (i) fluorine-containing fully substituted carbon centers could be readily assembled; (ii) no transition-metal catalyst was required; (iii) nucleophilic fluorination using cost-effective reagent was developed; (iv) the incorporation of aryl and fluorine substituents was orchestrated in a highly selective manner.

Initial attempt was carried out using 1,1-diphenylethylene 1a and aryldiazonium salt 2a with Et₃N·3HF as nucleophilic fluorination reagent. To our delight, when a mixture of 1a (0.1 mmol), 2a (0.2 mmol), and Et₃N·3HF(0.3 mmol) in CH₃CN (1.0 mL) was irradiated with 15 W blue LEDs for 12 h, 62% yield of the fluoroarylation product 3aa could be obtained (Table 1, entry 1). To further facilitate this transformation, a set of solvents such as THF, dioxane, DMF, etc. were subsequently screened, albeit with no positive results (Table 1, entries 2-4). Further interrogation of the fluorination reagent revealed the superiority of Et₃N·3HF, with other alternatives all leading to depressed reaction efficiencies (Table 1, entries 5-7). Notably, the addition of exogenous photoredox catalyst proved to be unprofitable, with unexpected attenuation of reaction yield being observed, in contrary (Table 1, entry 8). When changing the stoichiometry of 2a applied, however, no further increase in the yield of 3aa could be materialized.²⁰ It is delightful to find that an obvious enhancement of reaction turnover was eventually realized when reducing the amount of solvent while reversing the stoichiometric ratio of 1a and 2a (Table 1, entries 9-11). Control experiments further underscored the importance of reaction time, nitrogen atmosphere protection, as well as conducive effect of visible light irradiation, beyond simply acting as a heat source, on the present transformation.²⁰

With the optimal reaction conditions in hand, the reaction scope with respect to styrene derivative was subsequently investigated (Scheme 2). Delightfully, halogen substituents such as F, Cl, and Br, which provide the possibility for further

Table 1. Optimization of Reaction Conditions^a

Ph	2h 1a	+ EtO ₂ C	Et ₃ N•3HF MeCN, N ₂ , rt, 12 h 15 W blue LEDs	Ph F Ph 3aa	CO2Et
entry		vari	ation		yield (%) ^b
1		no			62, trace ^c
2		THF			24
3		dioxane			38
4		DMF, DMSO			trace
5		TMAF (10.0 equiv)			18
6		DMPU·HF (10.0 equiv))		NDP
7		pyridine·HF (10.0 equiv	7)		trace
8		2.5 mol % Ru(bpy) ₃ (PF	(₆) ₂ added		38
9		MeCN (0.5 mL)			65
10		1a (0.2 mmol), 2a (0.1	mmol)		74
11		MeCN (0.5 mL), 1a (0.2 mmol), 2a (0.1 mmol)			80 (79^d)

^{*a*}Unless otherwise noted, the reaction was conducted with **1a** (0.1 mmol), **2a** (0.2 mmol), and Et₃N·3HF (3.0 equiv) in MeCN (1.0 mL) under 15 W blue LEDs for 12 h. ^{*b*}Yield was determined by ¹⁹F NMR with 1-iodo-4-(trifluoromethyl)benzene as the internal standard. ^{*c*}At air atomosphere. ^{*d*}Isolated yield.



^{*a*}Unless otherwise noted, the reaction was conducted with 1 (0.2 mmol), **2a** (0.1 mmol), and $\text{Et}_3\text{N}\cdot3\text{HF}$ (3.0 equiv) in MeCN (0.5 mL) under irradiation of 15 W blue LEDs for 12 h. ^{*b*}0.3 mL DCE was added. ^{*c*}Yield was determined by ¹⁹F NMR with 1-iodo-4-(trifluoromethyl)benzene as the internal standard.

derivatization through traditional cross-coupling protocols, proved to be well tolerated, thus affording the desired products in good yields (3ba, 3ca, 3ea). Pleasingly, α -Me-styrene derivatives containing various substitutes were also compatible to this transformation, delivering the desired products in moderate to good yields (3ga-3na). It is worth noting that, in the case of substrates containing extra π -systems, the fluoroarylation occurred selectively on a more electron-rich position as showcased in examples of 3ka and 3la. To further probe the influence of substituents on the α -position of styrene derivatives, substrates decorated with n-Bu, Bn, Cy, cyclopentyl, and functionalized alkyl substituents containing remote unsaturated π -system or chlorine atom were examined and afforded 30a-3ta in good yields. To further showcase the generality of this protocol, cyclic styrene derivatives with exocyclic double bonds were subjected to the standard reaction conditions, which enabled a smooth assembly of structural motifs with cyclic fluorine-containing fully substituted carbon centers (3ua-3wa). Of note, the extension of this reaction to α_{β} -disubstituted styrene derivatives was also feasible, which delivered the corresponding products in moderate yields but with low diastereocontrol (3xa-3za, 3aaa).

Subsequently, the reaction generality with regard to aryldiazonium salts was surveyed (Scheme 3). Halogen



^{*a*}Unless otherwise noted, the reaction was conducted with 1 (0.2 mmol), 2 (0.1 mmol), and $Et_3N\cdot 3HF$ (3.0 equiv) in 0.5 mL MeCN under irradiation of 15 W blue LEDs for 12 h. ^{*b*}Yield was determined by ¹⁹F NMR with 1-iodo-4-(trifluoromethyl)benzene as the internal standard. ^{*c*}1.0 mL MeCN and 0.5 mL DCE was used as the solvent. ^{*d*}0.3 mL DCE was added.

atoms such as F, Cl, and Br were well compatible in this transformation, delivering products 3mb-3md in moderate yields. Aryldiazonium salts bearing synthetically useful groups such as ester, carbonyl, CF₃, CN, and NO₂ successfully participated in this reaction and gave the desired products in up to 84% yield (3ge-3gn). Notably, aryldiazonium salts with electro-donating/neutral substituents were also amenable despite the efficiency being somewhat attenuated, thus providing products in moderate yields (3go-3mq). Moreover, ethynyl-decorated substrate 2r was also competent and afforded product 3mr in 41% yield, with the alkyne group remaining intact throughout the reaction. Additionally, heteroarene-based substrates such as those derived from

quinolone and benzothiazole engaged in this reaction readily to furnish the desired producst 3gs and 3mt in 50% and 60% yields, respectively. To further exemplify the applicability of this protocol, aryldiazonium salts derived from coumarin, Lmenthol, and vitamin E were then tested, which delivered respective products without compromising reaction yields (3gu-3gw).

To gain insight into the reaction mechanism of the present Meerwein fluoroarylation process, a panel of control experiments were implemented. Initially, when styrenes 1a' and 1a''devoid of α -substituent were subjected to the standard reaction conditions, no fluoroarylation products could be acquired, thus indicating that single electron transfer (SET) between secondary benzylic radical intermediates, as involved in these cases, with an aryldiazonium salt tend to be an inefficient process (Scheme 4a). It is worth pointing out that





fluoroarylation product of 1a' could be obtained, albeit in 11% yield, via the Heinrich protocol by leveraging the radical type fluorine atom transfer with the electrophilic fluorination reagent.^{6d} We assume that the key to the amenability of monosubstituted styrene derivative resides in disclosing an efficient radical-polar crossover manifold regarding the secondary radical intermediate. Therefore, the photocatalyst was further examined in the reaction of 1a'. Pleasingly, the fluoroarylation product 3a'a could be obtained in 22% yield when $Ir(ppy)_3$ was used as the catalyst, and this modification also enabled the formation of product 3a"a in 30% yield for substrate 1a" (Scheme 4a). To further challenge the generality of the present reaction, aliphatic alkene lab was interrogated under standard reaction conditions; however, no desired product could be obtained (Scheme 4b). Furthermore, when cyclopropyl-decorated styrene substrate lac was employed, the fluoroarylation proceeded uneventfully to afford product 3aca in 69% yield, with the cyclopropyl group being unscathed (Scheme 4c). Meanwhile, when Ph-substituted analogue 1ad

was employed, the anticipated radical ring-opening fluorination product 3ada could be obtained in 19% yield in the presence of photoredox catalyst Ir(ppy)₃(Scheme 4d). In order to further prove the radical nature of this reaction, the model reaction was tested in the presence of TEMPO, which resulted in a dramatic impediment of reaction turnover, thus suggesting the involvement of radical species in this transformation (Scheme 4e). Additionally, we also inspected the reaction between 1a and 2a but with the absence of $Et_3N.3HF$, which delivered Meerwein arylation product 4aa in 30% vield. However, further submitting 4aa to the standard reaction conditions gave no formation of desired product 3aa, which firmly precluded the involvement of 4aa as the key intermediate in the present transformation (Scheme 4f). Finally, to demonstrate the practicality of the present fluoroarylation protocol, a scale-up reaction at 1.0 mmol was also conducted, which led to the formation of 3aa in 70% yield.²⁰

Given all experimental investigations above, we tentatively proposed a possible reaction mechanism (Scheme 5). The

Scheme 5. Proposed Mechanism



reaction initiation was based on the generation of aryl radical I by aryldiazonium salt 2, which is a well-known process that is promoted by light irradiation.^{15d} Then the nascent aryl radical I further underwent regioselective homolytic addition to styrene derivatives to afford tertiary benzyl radical II. The following SET between benzyl radical II and aryldiazonium salt 2 would readily produce the carbonium intermediate III accompanied by the regeneration of aryl radical I, which could effectively propagate the turnover by reentering the productive cycle. Meanwhile, the nucleophilic fluorination of species III by Et₃N·3HF smoothly provided the final product 3.

In summary, we have developed a novel photoinduced Meerwein-type fluoroarylation of styrene derivatives with readily available aryldiazonium salts and a cost-effective nucleophilic fluorination reagent. This transformation was characterized by its practical operation and atom-economic and mild reaction conditions. Using this protocol, a host of 1,1diarylethane derivatives bearing fluorine-containing fully substituted carbon centers were readily synthesized. The use of aryldiazonium salts as both an aryl donor and single-electron acceptor was critical for a smooth transformation without recourse to transition-metal catalysts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01249.

Optimization, experimental procedures; compound characterization (¹H NMR, ¹³C NMR, and HRMS); ¹H NMR and ¹³C NMR reprints (PDF)

AUTHOR INFORMATION

Corresponding Author

Chao Feng – Technical Institute of Fluorochemistry (TIF), Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, P. R. China; orcid.org/0000-0003-4494-6845; Email: iamcfeng@njtech.edu.cn

Authors

- Hai-Jun Tang Technical Institute of Fluorochemistry (TIF), Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, P. R. China
- Bin Zhang Technical Institute of Fluorochemistry (TIF), Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing 211816, P. R. China
- Fei Xue Institute of Material Physics & Chemistry, College of Science, Nanjing Forestry University, Nanjing 210037, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.1c01249

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of the National Natural Science Foundation of China (21871138) and the Natural Science Foundation of Jiangsu Province (BK20170984), the "Thousand Talents Plan" Youth Program, the "Jiangsu Specially-Appointed Professor Plan", and the "Innovation & Entrepreneurship Talents Plan".

REFERENCES

(1) (a) O'Hagan, D.; Harper, D. B. Fluorine-Containing Natural Products. J. Fluorine Chem. **1999**, 100, 127–133. (b) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. Fluorine in Medicinal Chemistry. Chem. Soc. Rev. **2008**, 37, 320–330. (c) Berger, R.; Resnati, G.; Metrangolo, P.; Weber, E.; Hulliger, J. Organic Fluorine Compounds: a Great Opportunity for Enhanced Materials Properties. Chem. Soc. Rev. **2011**, 40, 3496–3508.

(2) Szpera, R.; Moseley, D. F. J.; Smith, L. B.; Sterling, A. J.; Gouverneur, V. The Fluorination of C-H Bonds: Developments and Perspectives. *Angew. Chem., Int. Ed.* **2019**, *58*, 14824–14848.

(3) For selected reports on fluoroalkylation of olefins: (a) Deng, W.; Feng, W.; Li, Y.; Bao, H. Merging Visible-Light Photocatalysis and Transition-Metal Catalysis in Three-Component Alkyl-Fluorination of Olefins with a Fluoride Ion. Org. Lett. **2018**, 20, 4245–4249. (b) Li, C.-G.; Xie, Q.; Xu, X.-L.; Wang, F.; Huang, B.; Liang, Y.-F.; Xu, H.-J. Silver-Catalyzed Decarboxylative Alkylfluorination of Alkenes. Org. Lett. **2019**, 21, 8496–8500. (c) Sim, J.; Campbell, M. W.; Molander, G. A. Synthesis of α -Fluoro- α -amino Acid Derivatives via Photoredox-Catalyzed Carbofluorination. ACS Catal. **2019**, 9, 1558–1563.

(4) For selected reports on fluorotrifluoromethylation of olefins: (a) Yu, W.; Xu, X.-H.; Qing, F.-L. Silver-Mediated Oxidative Fluorotrifluoromethylation of Unactivated Alkenes. *Adv. Synth. Catal.* **2015**, 357, 2039–2044. (b) Liu, Z.; Chen, H.; Lv, Y.; Tan, X.; Shen, H.; Yu, H.-Z.; Li, C. Radical Carbofluorination of Unactivated Alkenes with Fluoride Ions. J. Am. Chem. Soc. 2018, 140, 6169-6175.

(5) Xiong, P.; Long, H.; Xu, H.-C. Electrochemical Fluoroalkynylation of Aryl Alkenes with Fluoride Ions and Alkynyltrifluoroborate Salts. *Asian J. Org. Chem.* **2019**, *8*, 658–660.

(6) For selected examples of fluoroarylation of unsaturated π systems: (a) Wolstenhulme, J. R.; Rosenqvist, J.; Lozano, O.; Ilupeju, J.; Wurz, N.; Engle, K. M.; Pidgeon, G. W.; Moore, P. R.; Sandford, G.; Gouverneur, V. Asymmetric Electrophilic Fluorocyclization with Carbon Nucleophiles. *Angew. Chem., Int. Ed.* **2013**, *52*, 9796–9800. (b) Braun, M.-G.; Katcher, M. H.; Doyle, A. G. Carbofluorination via a Palladium-Catalyzed Cascade Reaction. *Chem. Sci.* **2013**, *4*, 1216–1220. (c) Talbot, E. P. A.; Fernandes, T. de A.; McKenna, J. M.; Toste, F. D. Asymmetric Palladium-Catalyzed Directed Intermolecular Fluoroarylation of Styrenes. *J. Am. Chem. Soc.* **2014**, *136*, 4101–4104. (d) Pirzer, A. S.; Alvarez, E.-M.; Friedrich, H.; Heinrich, M. R. Radical Carbofluorination of Alkenes with Arylhydrazines and Selectfluor: Additives, Mechanistic Pathways, and Polar Effects. *Chem. - Eur. J.* **2019**, *25*, 2786–2792 and references cited therein.

(7) Qi, X.; Yu, F.; Chen, P.; Liu, G. Intermolecular Palladium-Catalyzed Oxidative Fluorocarbonylation of Unactivated Alkenes: Efficient Access to β -Fluorocarboxylic Esters. *Angew. Chem., Int. Ed.* **2017**, 56, 12692–12696.

(8) (a) Dilman, A. D.; Belyakov, P. A.; Struchkova, M. I.; Arkhipov, D. E.; Korlyukov, A. A.; Tartakovsky, V. A. Fluorocyanation of Enamines. J. Org. Chem. 2010, 75, 5367–5370. (b) Liu, J.-L.; Zhu, Z.-F.; Liu, F. Cyanofluorination of Vinyl Ethers Enabled by Electron-Donor-Acceptor Complexes. Org. Chem. Front. 2019, 6, 241–244.

(9) Tian, P.; Wang, C.-Q.; Cai, S.-H.; Song, S.; Ye, L.; Feng, C.; Loh, T.-P. F⁻ Nucleophilic-Addition-Induced Allylic Alkylation. *J. Am. Chem. Soc.* **2016**, *138*, 15869–15872.

(10) Tang, H.-J.; Lin, L.-Z.; Feng, C.; Loh, T.-P. Palladium-Catalyzed Fluoroarylation of gem-Difluoroalkenes. Angew. Chem., Int. Ed. 2017, 56, 9872–9876.

(11) Tang, H.-J.; Zhang, X.; Zhang, Y.-F.; Feng, C. Visible-Light-Assisted Gold-Catalyzed Fluoroarylation of Allenoates. *Angew. Chem., Int. Ed.* **2020**, *59*, 5242–5247.

(12) Meerwein, H.; Büchner, E.; Emster, K. v. Über die Einwirkung Aromatischer Diazoverbindungen auf $\alpha_{,\beta}$ -Ungesättigte Carbonylverbindungen. J. Prakt. Chem. **1939**, 152, 237–266.

(13) Mastrorilli, P.; Nobile, C. F.; Taccardi, N. Chloride Based Ionic Liquids as Promoting Agents for Meerwein Reaction in Solventless Conditions. *Tetrahedron Lett.* **2006**, *47*, 4759–4762.

(14) Arylamination of alkenes based on Meerwein arylation: (a) Fumagalli, G.; Boyd, S.; Greaney, M. F. Oxyarylation and Aminoarylation of Styrenes Using Photoredox Catalysis. *Org. Lett.* **2013**, *15*, 4398–4401. (b) Prasad Hari, D.; Hering, T.; Konig, B. The Photoredox-Catalyzed Meerwein Addition Reaction: Intermolecular Amino-Arylation of Alkenes. *Angew. Chem., Int. Ed.* **2014**, *53*, 725– 728. (c) Kindt, S.; Wicht, K.; Heinrich, M. R. Base-Induced Radical Carboamination of Nonactivated Alkenes with Aryldiazonium Salts. *Org. Lett.* **2015**, *17*, 6122–6125.

(15) Aryloxygenation of alkenes based on Meerwein arylation: (a) Kindt, S.; Jasch, H.; Heinrich, M. R. Manganese(IV)-Mediated Hydroperoxyarylation of Alkenes with Aryl Hydrazines and Dioxygen from Air. *Chem. - Eur. J.* **2014**, *20*, 6251–6255. (b) Yao, C.-J.; Sun, Q.; Rastogi, N.; König, B. Intermolecular Formyloxyarylation of Alkenes by Photoredox Meerwein Reaction. *ACS Catal.* **2015**, *5*, 2935–2938. (c) Kindt, S.; Wicht, K.; Heinrich, M. R. Thermally Induced Carbohydroxylation of Styrenes with Aryldiazonium Salts. *Angew. Chem., Int. Ed.* **2016**, *55*, 8744–8747. (d) Altmann, L.-M.; Zantop, V.; Wenisch, P.; Diesendorf, N.; Heinrich, M. R. Visible Light Promoted, Catalyst-Free Radical Carbohydroxylation and Carboetherification under Mild Biomimetic Conditions. *Chem. - Eur. J.* **2021**, *27*, 2452–2462.

(16) Hari, D. P.; Hering, T.; König, B. Visible Light Photocatalytic Synthesis of Benzothiophenes. *Org. Lett.* **2012**, *14*, 5334–5337.

(17) Aryl halides converted into aryl radicals: (a) Chatgilialoglu, C. (Me₃Si)₃SiH: Twenty Years After Its Discovery as a Radical-Based

Reducing Agent. *Chem. - Eur. J.* **2008**, *14*, 2310–2320. (b) Liu, Q.; Han, B.; Zhang, W.; Yang, L.; Liu, Z.-L.; Yu, W. Photo-Induced Radical Cyclization of Aromatic Halides with Sodium Borohydride. *Synlett* **2005**, 2248–2250.

(18) (a) Cahard, D.; Xu, X.; Couve-Bonnaire, S.; Pannecoucke, X. Fluorine & Chirality: How to Create a Nonracemic Stereogenic Carbon-Fluorine Center. *Chem. Soc. Rev.* **2010**, *39*, 558–568. (b) Zhu, Y.; Han, J.; Wang, J.; Shibata, N.; Sodeoka, M.; Soloshonok, V. A.; Coelho, J. A. S.; Toste, F. D. Modern Approaches for Asymmetric Construction of Carbon-Fluorine Quaternary Stereogenic Centers: Synthetic Challenges and Pharmaceutical Needs. *Chem. Rev.* **2018**, *118*, 3887–3964.

(19) (a) Zhang, Y.; Liu, H.; Tang, L.; Tang, H.-J.; Wang, L.; Zhu, C.; Feng, C. Intermolecular Carboamination of Unactivated Alkenes. J. Am. Chem. Soc. **2018**, 140, 10695–10699. (b) Ge, L.; Wang, D.-X.; Xing, R.; Ma, D.; Walsh, P. J.; Feng, C. Photoredox-Catalyzed Oxo-Amination of Aryl Cyclopropanes. Nat. Commun. **2019**, 10, 4367– 4375. (c) Liu, H.; Ge, L.; Wang, D.-X.; Chen, N.; Feng, C. Photoredox-Coupled F⁻ Nucleophilic Addition: Allylation of gem-Difluoroalkenes. Angew. Chem., Int. Ed. **2019**, 58, 3918–3922.

(20) See the Supporting Information for details.