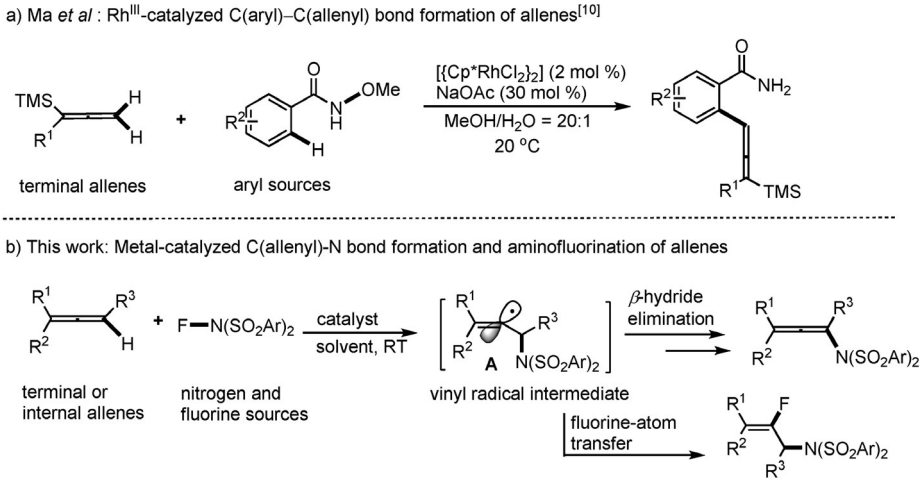
Allenes

International Edition: DOI: 10.1002/anie.201506066
German Edition: DOI: 10.1002/ange.201506066

Highly Regioselective Radical Amination of Allenes: Direct Synthesis of Allenamides and Tetrasubstituted Alkenes

*Ge Zhang, Tao Xiong, Zining Wang, Guoxing Xu, Xuedan Wang, and Qian Zhang**

Abstract: *The first controllable, regioselective radical amination of allenes with N-fluoroarylsulfonimide is described to proceed under very mild reaction conditions. With this methodology, a general and straightforward route for the synthesis of both allenamides and fluorinated tetrasubstituted alkenes was realized from a wide range of terminal and internal allenes.*

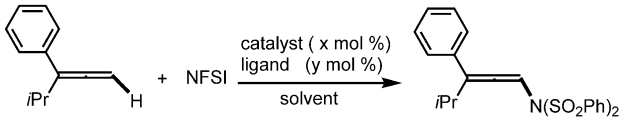


Scheme 1. Direct arylation, oxidative amination, and aminofluorination of allenes. Cp* = C_5Me_5, TMS = trimethylsilyl.

The allenamide motif represents one of the most versatile synthetic building blocks in a variety of synthetic transformations and is excellent precursor in natural product synthesis.[1] It is also displayed in some anti-HIV-1 and anti-hepatitis-B virus agents within the pharmaceutical field.[2] Accordingly, the synthesis of these versatile units has attracted intensive research interest, thus resulting in a variety of strategies towards its construction, including base-induced isomerization of propargyl amides,[3] sigmatropic rearrangements,[4] elimination reactions of enol triflates, and propargyl phosphonium ether.[5] In addition, the transition-metal-catalyzed intramolecular amino-cyclizations[6] and Trost–Hsung *N*-allenylation[7] methods have also been developed in recent years. Nevertheless, most of the current methods suffer from at least one of the following drawbacks: harsh reaction conditions (such as use of strong bases, high temperature), the requirement of prefunctionalization of substrates, or employment noble metals. Hence, a general, mild, and efficient approach to the synthesis of allenamides is highly desired.

Transition-metal-catalyzed C–H amination has emerged as a straightforward and economical protocol in chemical synthesis. Accordingly, enormous efforts have been devoted to this reaction and impressive progress has been achieved in recent years.[8] However, direct C–H amination protocols of highly reactive allenes[9] to afford amino-substituted allenes

Table 1: Optimization of reaction conditions.[a]

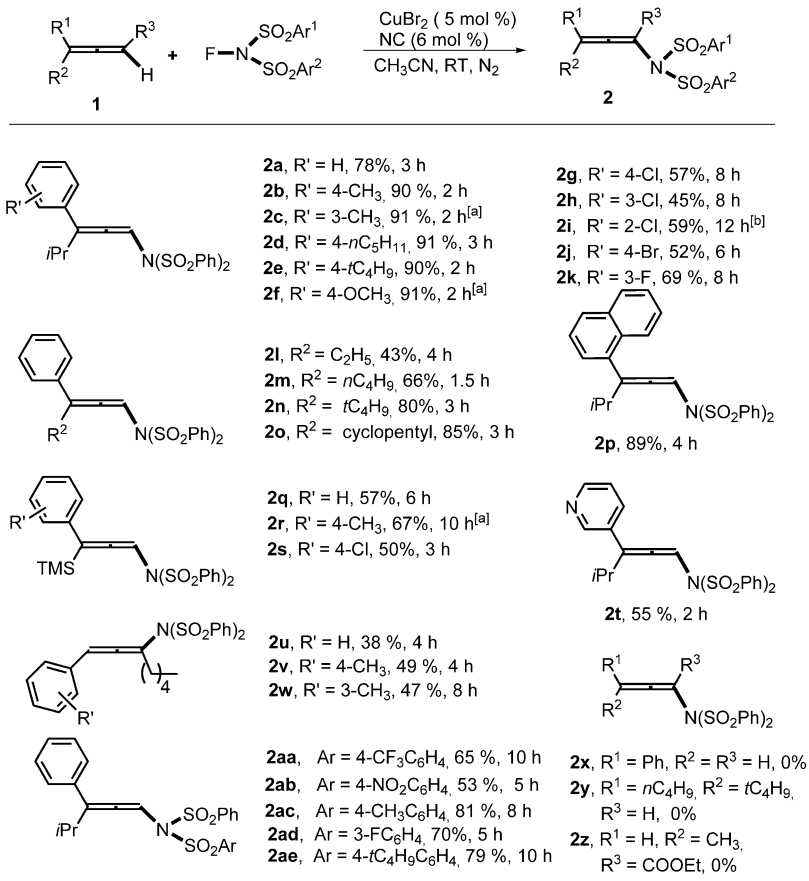


Entry	Catalyst (mol%)	Ligand (mol%)	Solvent	Yield [%]
1	CuCl (5)	none	CH_3CN	31
2	CuTc (5)	none	CH_3CN	21
3	$CuBr_2$ (5)	none	CH_3CN	47
4	$Cu(OTf)_2$ (5)	none	CH_3CN	25
5	$CuBr_2$ (5)	none	DCE	32
6	$CuBr_2$ (5)	none	toluene	28
7	$CuBr_2$ (5)	none	THF	trace
8	$CuBr_2$ (5)	Phen (6)	CH_3CN	67
9	$CuBr_2$ (5)	BC (6)	CH_3CN	66
10	$CuBr_2$ (5)	NC (6)	CH_3CN	72
11	$CuBr_2$ (5)	BPy (6)	CH_3CN	40
12	$CuBr_2$ (5)	NC (6)	CH_3CN	82[b]
13	$CuBr_2$ (5)	NC (6)	CH_3CN	78[c]

[a] Reaction was performed with 1.3 equiv of **1a**, 0.2 mmol NFSI, 5 mol% catalyst, and 6 mol% ligand in 2 mL of solvent at 50 °C under N_2 for 3 h unless otherwise stated. [b] 0.2 mmol **1a**, 1.3 equiv of NFSI were employed. [c] Reaction was performed at room temperature for 5 h. BC = bathocuproine, BPy = 2,2′-bipyridine, DCE = 1,2-dichloroethane, Phen = 1,10-phenanthroline, NC = neocuproine, Tf = trifluoromethanesulfonyl, THF = tetrahydrofuran.

[*] G. Zhang,[+] Prof. T. Xiong,[+] Z. Wang, G. Xu, X. Wang, Prof. Q. Zhang
Department of Chemistry, Northeast Normal University
Changchun, 130024 (China)
E-mail: Zhangq651@nenu.edu.cn
[+] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201506066.



Scheme 2. Direct oxidative coupling of the C(sp^2)–H bond of allenes with *N*-fluoroarylsulfonimides. Reaction was performed with 0.2 mmol of **1**, 1.3 equiv *N*-fluoroarylsulfonimide, 5 mol% catalyst, and 6 mol% ligand in 2 mL solvent at RT under N_2, unless otherwise stated. Yield is that of the isolated product. [a] The reaction was performed at −15 °C. [b] The reaction was performed at 50 °C.

remains elusive. Challenges mainly result from: 1) control of the regioselectivity for C–N bond formation at either the terminal or central allenic carbon atom; 2) thermally disfavored processes for the formation of higher-energy substituted allene products as compared to aminodifunctionlization of allenes. Recently, Ma and co-workers developed a mild rhodium(III)-catalyzed C(aryl)–C(allenyl) bond-forming reaction of geminal-disubstituted allenes with *N*-methoxybenzamides through a Heck-type process, and the arylation of allenes was realized by utilizing the bulk of the silyl group to promote β-hyride elimination (Scheme 1 a).[10]

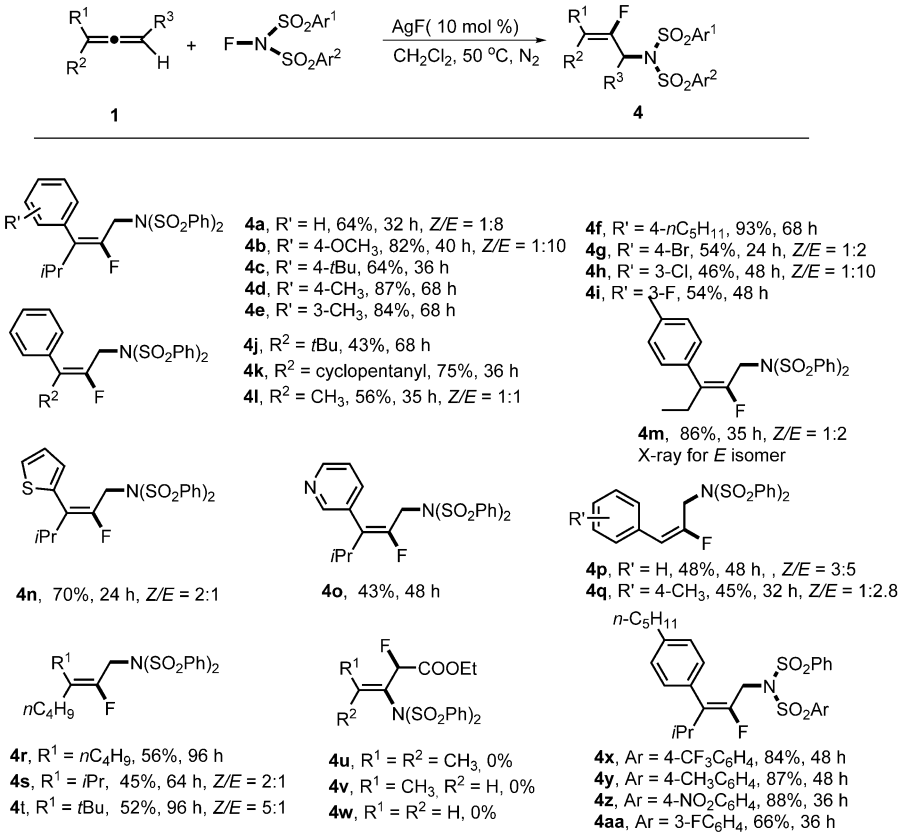
A number of efficient transformations based on allenes have been successfully realized,[9] however, mild and regioselective radical reactions of allenes are far less developed.[11] More recently, we realized a general radical cascade reaction of an alkyne with *N*-fluoroarylsulfonimide and an alcohol, during which a key nitrogen radical addition to the alkyne, for the formation of vinyl radical intermediate, was involved.[12a] The vinyl radical intermediate **A** (Scheme 1 b) led us to test the challenging regioselective radical amination reaction of allenes with *N*-fluoroarylsulfonimide. It has been demonstrated that starting from *N*-fluorobenzenesulfonimide (NFSI), a sterically hindered metal-stabilized nitrogen radical species could be generated under mild reaction conditions.[12] Herein, by employing an inexpensive copper catalyst, we report the first example of the highly regioselective C–H amination of allenes by a radical process which generates various allenamides from both terminal and internal allenes. In addition, with silver as the catalyst, aminofluorination of allenes for fluorinated polysubstituted alkenes was also realized (Scheme 1 b).

To test our hypothesis on the amination of allenes, we initially employed copper salts as the catalysts and NFSI as the nitrogen source.[12,13] We were pleased to find that treatment of 1.3 equivalents of the 1,1-disubsitituted allene **1a** with 5 mol% CuCl and NFSI in CH_3CN at 50 °C for 3 hours under a N_2 atmosphere gave amination product **2a** in 31% yield with high regioselectivity (Table 1, entry 1). Other copper(I) and copper(II) catalysts were also investigated and $CuBr_2$ was identified as the most efficient catalyst for this transformation (entries 2–4). Among the solvents screened, CH_3CN was found to be optimal (entries 5–7). To further improve the yield, we turned our attention to screening ligands.[14] Thus, various mono-, bi-, and tridentate nitrogen-containing ligands were investigated, and the best yield (72%) was afforded with neocuproine (NC) as the ligand (entries 8–11). Moreover, by increasing the ratio of NFSI to allene, the yield was further improved (entry 12). To our delight, the desired amination product was isolated in 78% yield when the reaction was run at room temperature (entry 13), and the reaction conditions were thus defined as the standard reaction conditions for subsequent investigations. In the absence of the copper catalyst, no amination product was observed. A comprehensive list of screening data is presented in the Supporting Information.

With the optimized reaction conditions (Table 1, entry 13), we next explored the scope and limitations of the process with respect to the allenes and nitrogen sources, and the results are summarized in Scheme 2. Gratifyingly, the allenes **1b–k**, bearing either electron-donating or electron-withdrawing groups on arenes, participated in this highly regioselective amination reaction to provide **2b–k** in moderate to excellent yields. The substrates with aryl groups displaying electron-withdrawing substituents (**1g–k**) resulted in lower product yields, and bromoamination and aminofluorination byproducts of allenes, as well as $NH(SO_2Ph)_2$, resulting from the decomposition of NFSI, were observed. In addition, *ortho*-, *meta*-, and *para*-substituents on the aromatic ring of the allenes **1g–i** were viable substrates for these transformations, thus affording the desired amination products in moderate yields. When the ethyl-substituted substrate **1l** was applied, **2l** was obtained in 43% yield. Next, we investigated the linear and branched alkyl-substituted sub-

strates **1m** and **1n**, and results showed that **1n**, having a more bulky substituent, is more efficient.[10] The cyclopentyl substrate **1o** and naphthyl-substituted allene **1p** are also effective. It is worthy to note that the synthetically more attractive silyl motif, which is sensitive to oxidants and fluorides, also survived the reaction conditions and the desired amination products **2q**, **2r**, and **2s** were afforded in 50–67% yields. The more challenging substrate **1t**, bearing a strongly coordinating pyridine moiety,[15] also worked well and delivered **2t** in 55% yield. Remarkably, the unsymmetrical 1,3-disubstituted allenes were found to be suitable for the amination reaction and delivered the corresponding allenamides **2u**–**w** in acceptable yields, with the nitrogen atom being attached to the less sterically hindered terminal allenic carbon atom. The structure of **2v** was further confirmed by a NOESY experiment. The monosubstituted allene **1x** and geminal-dialkyl-substituted allene **1y** were not suitable substrates under the optimal reaction conditions, and thus provided complex mixtures. Additionally, the allene **1z**, bearing an electron-withdrawing ester group, was intact in this transformation. Finally, various N-F reagents bearing either strong electron-withdrawing groups (F, -CF_3, -NO_2) or electron-rich groups on aromatic rings also furnished allenamides (**2aa**–**ae**) in 53–81% yields under this mild catalytic reaction. The potential mechanism of this direct amination of allene is discussed in the Supporting Information.

The unique properties of the fluorine atom render fluorine-containing compounds useful for applications in agrochemistry, the pharmaceutical industry, materials science, and as radiotracers for positron emission tomography (PET).[16] Also, a limited number of structurally simple fluorine-containing compounds exist as natural products.[17] These facts stimulated the development of efficient, selective, and general methodologies for the formation of C–F bonds. Among them, both nucleophilic and electrophilic fluorinations have made considerable advances in recent years. However, radical fluorination under benign reaction conditions is far less explored, especially for the construction of C(vinyl)–F bonds.[18] Based on the above experimental results for the facile formation of the vinyl intermediate **A** (Scheme 1b), and our previous strategy,[12a] as well as the well-established silver-catalyzed radical fluorination by fluorine-atom-transfer protocols,[19] we envisioned that a combination of a silver catalyst, an N–F reagent, and allenes might be utilized to access the fluorinated polysubstituted alkenes by a highly regioselective radical aminofluorination process of allenes. To our knowledge, this radical transformation still remains a significant challenge and only one example has been disclosed for the intermolecular radical aminofluorination process of allene with N_2F_4 in the gas phase.[20] Additionally, it is difficult to synthesize tetrasubstituted alkenes bearing four different carbon-linked groups because of the congested nature of the unsaturated bond.[21] Therefore, we set out to explore our hypothesis. Indeed, when the reaction was carried out in dichloromethane at the 50 °C with AgF as the catalyst, we were delighted to see that the expected aminofluorination product **4a** was observed in 64% yield as isolated as the major product with an 8:1 stereoselectivity (Scheme 3).[22] The data presented shows the scope of the developed radical aminofluorination of allenes for the synthesis of a wide range of fluorinated polysubstituted alkenes. In general, various of 1,1-disubstituted allenes reacted smoothly and provided the desired products in 43–93% yields. Allenes with an electron-donating groups on the aromatic ring (**4a**–**f**) were more efficient than substrates bearing electron-withdrawing groups (**4g**–**i**), and $NH(SO_2Ph)_2$ was the major byproduct obtained in some cases. For example, 17% and 31% $NH(SO_2Ph)_2$ was isolated during the transformations of **1g** into **4g** and **1i** into **4i**, respectively, under standard reaction conditions. Additionally, the stereochemistry profile of our method was significantly influenced



Scheme 3. Silver-catalyzed aminofluorination of allenes. Reaction was performed with 2.0 equiv of **1**, 0.3 mmol *N*-fluoroarylsulfonimide, 10 mol% catalyst in 3 mL solvent at RT under N_2, unless otherwise stated. Yield is that of the isolated product. The *E*/*Z* ratio was determined by ^{1}H NMR spectroscopy.

by the sterics of the substituents. Bulky alkyl-substituted allenes exhibited exclusive stereoselectivity (**4j**, **4k**), while methyl- and ethyl-substituted allenes resulted in low stereoselectivity (**4l**, **4m**). Notably, the allene bearing either a thiophene or pyridine moiety was well tolerated and delivered the targets **4n** (70%) and **4o** (43%), respectively. Furthermore, monosubstituted allenes were suitable substrates for these transformations (**4p**, **4q**). In addition, geminal-dialkyl-substituted allenes were successfully transformed into the corresponding aminofluorination products **4r–t** with acceptable yields. The electron-deficient allenes **1u–w** did not react with NFSI under the optimal reaction conditions, even when the reaction was run at 100 °C. Finally, various N-F reagents showed good reactivity and afforded the desired products in 66%-88% yields (**4x–4aa**). Some additional experimental results for preliminary mechanistic investigations and the possible mechanism for this aminofluorination process are provided in the Supporting Information.

In summary, the first example of the highly regioselective oxidative amination of allenes with *N*-fluoroarylsulfonimides has been developed. In addition, by tuning the metal catalyst, aminofluorination products were also be realized. As a result, general and efficient approaches for the synthesis of the versatile allenamides and fluorinated polysubstituted alkenes are provided. These transformations proceed at very mild conditions and show good tolerance of many synthetically attractive functionalities. Additional investigations to expand the scope with respect to the substrates, as well as to clarify the reaction mechanism, are currently underway in our laboratory.

Acknowledgements

Financial support of this research from the NNSFC (21202014, 21372041, 21172033) and SRFDP (20120043120009) are greatly acknowledged.

Keywords: allenes · copper · fluorine · radicals · transition metals

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 12649–12653
Angew. Chem. **2015**, *127*, 12840–12844

[1] a) T. Lu, Z. Lu, Z.-X. Ma, Y. Zhang, R. P. Hsung, *Chem. Rev.* **2013**, *113*, 4862–4904; b) L.-l. Wei, H. Xiong, R. P. Hsung, *Acc. Chem. Res.* **2003**, *36*, 773–782; c) A. Navarro-Vázquez, D. Rodríguez, M. F. Martínez-Esperón, A. García, C. Saá, D. Domínguez, *Tetrahedron Lett.* **2007**, *48*, 2741–2743; d) J. E. Antoline, R. P. Hsung, J. Huang, Z. Song, G. Li, *Org. Lett.* **2007**, *9*, 1275–1278; e) Z. Song, R. P. Hsung, *Org. Lett.* **2007**, *9*, 2199–2202; f) Z. Song, R. P. Hsung, T. Lu, A. G. Lohse, *J. Org. Chem.* **2007**, *72*, 9722–9731; g) R. Hayashi, Z.-X. Ma, R. P. Hsung, *Org. Lett.* **2012**, *14*, 252–255.

[2] a) A. Hoffmann-Röder, N. Krause, *Angew. Chem. Int. Ed.* **2004**, *43*, 1196–1216; *Angew. Chem.* **2004**, *116*, 1216–1236; b) S. Hayashi, S. Phadtare, J. Zemlicka, M. Matsukura, H. Mitsuya, S. Broder, *Proc. Natl. Acad. Sci. USA* **1988**, *85*, 6127–6131; c) S. Phadtare, J. Zemlicka, *J. Am. Chem. Soc.* **1989**, *111*, 5925–5931; d) S. Phadtare, D. Kessel, T. H. Corbett, H. E. Renis, B. E. Court, J. Zemlicka, *J. Med. Chem.* **1991**, *34*, 421–429; e) B. C. N. M. Jones, J. V. Silverton, C. Simons, S. Megati, H. Nishimura, Y. Maeda, H. Mitsuya, J. Zemlicka, *J. Med. Chem.* **1995**, *38*, 1397–1405; f) S. Megati, Z. Goren, J. V. Silverton, J. Orlina, H. Nishimura, T. Shirasaki, H. Mitsuya, J. Zemlicka, *J. Med. Chem.* **1992**, *35*, 4098–4104.

[3] a) W. B. Dickinson, P. C. Lang, *Tetrahedron Lett.* **1967**, *8*, 3035–3040; b) A. Padwa, T. Caruso, S. Nahm, A. Rodriguez, *J. Am. Chem. Soc.* **1982**, *104*, 2865–2871; c) I. Fenández, M. I. Monterde, J. Plumet, *Tetrahedron Lett.* **2005**, *46*, 6029–6031; d) D. R. Garud, H. Ando, Y. Kawai, H. Ishihara, M. Koketsu, *Org. Lett.* **2007**, *9*, 4455–4458; e) L. J. van Boxtel, S. Körbe, M. Noltemeyer, A. de Meijere, *Eur. J. Org. Chem.* **2001**, 2283–2292; f) J. Huang, H. Xiong, R. P. Hsung, C. Rameshkumar, J. A. Mulder, T. P. Grebe, *Org. Lett.* **2002**, *4*, 2417–2420.

[4] a) K. K. Balasubramanian, B. Venugopalan, *Tetrahedron Lett.* **1974**, *15*, 2643–2644; b) K. K. Balasubramanian, B. Venugopalan, *Tetrahedron Lett.* **1974**, *15*, 2645–2648; c) L. E. Overman, L. A. Clizbe, R. L. Freerks, C. K. Marlowe, *J. Am. Chem. Soc.* **1981**, *103*, 2807–2815; d) N. A. Romero, B. M. Klepser, C. E. Anderson, *Org. Lett.* **2012**, *14*, 874–877; e) A. M. Danowitz, C. E. Taylor, T. M. Shrikian, A. K. Mapp, *Org. Lett.* **2010**, *12*, 2574–2577; f) G. Yin, Y. Zhu, L. Zhang, P. Lu, Y. Wang, *Org. Lett.* **2011**, *13*, 940–943.

[5] a) H. Tanaka, Y. Kameyama, S.-i. Sumida, T. Yamada, Y. Tokumaru, T. Shiroi, M. Sasaoka, M. Taniguchi, S. Torii, *Synlett* **1991**, 888–890; b) V. Farina, J. Kant, *Tetrahedron Lett.* **1992**, *33*, 3559–3562; c) M. D. Clay, A. G. Fallis, *Angew. Chem. Int. Ed.* **2005**, *44*, 4039–4042; *Angew. Chem.* **2005**, *117*, 4107–4110; d) I. T. Crouch, R. K. Neff, D. E. Frantz, *J. Am. Chem. Soc.* **2013**, *135*, 4970–4973.

[6] a) M. Kimura, Y. Wakamiya, Y. Horino, Y. Tamaru, *Tetrahedron Lett.* **1997**, *38*, 3963–3966; b) Y. Kozawa, M. Mori, *Tetrahedron Lett.* **2001**, *42*, 4869–4873; c) Y. Kozawa, M. Mori, *Tetrahedron Lett.* **2002**, *43*, 1499–1502.

[7] a) B. M. Trost, D. T. Stiles, *Org. Lett.* **2005**, *7*, 2117–2120; b) L. Shen, R. P. Hsung, Y. Zhang, J. E. Antoline, X. Zhang, *Org. Lett.* **2005**, *7*, 3081–3084; c) Y. Tang, L. Shen, B. J. Dellaria, R. P. Hsung, *Tetrahedron Lett.* **2008**, *49*, 6404–6409; d) A. K. Å. Persson, E. V. Johnston, J.-E. Bäckvall, *Org. Lett.* **2009**, *11*, 3814–3817.

[8] a) F. Collet, R. H. Dodd, P. Dauban, *Chem. Commun.* **2009**, 5061–5074; b) T. A. Ramirez, B. Zhao, Y. Shi, *Chem. Soc. Rev.* **2012**, *41*, 931–942; c) F. Collet, C. Lescot, P. Dauban, *Chem. Soc. Rev.* **2011**, *40*, 1926–1936; d) R. T. Gephart, T. H. Warren, *Organometallics* **2012**, *31*, 7728–7752; e) M.-L. Louillat, F. W. Patureau, *Chem. Soc. Rev.* **2014**, *43*, 901–910.

[9] a) R. Zimmer, C. U. Dinesh, E. Nandanan, F. A. Khan, *Chem. Rev.* **2000**, *100*, 3067–3126; b) S. Ma, *Chem. Rev.* **2005**, *105*, 2829–2872; c) M. Brasholz, H.-U. Reissig, R. Zimmer, *Acc. Chem. Res.* **2009**, *42*, 45–56; d) S. Ma, *Acc. Chem. Res.* **2009**, *42*, 1679–1688; e) B. Alcaide, P. Almendros, *Adv. Synth. Catal.* **2011**, *353*, 2561–2576; f) N. Krause, C. Winter, *Chem. Rev.* **2011**, *111*, 1994–2009; g) S. Yu, S. Ma, *Chem. Commun.* **2011**, *47*, 5384–5418; h) S. Yu, S. Ma, *Angew. Chem. Int. Ed.* **2012**, *51*, 3074–3112; *Angew. Chem.* **2012**, *124*, 3128–3167; i) W. Yang, A. S. K. Hashmi, *Chem. Soc. Rev.* **2014**, *43*, 2941–2955; j) M. P. Muñoz, *Chem. Soc. Rev.* **2014**, *43*, 3164–3183; k) C. Aubert, L. Fensterbank, P. Garcia, M. Malacria, A. Simonneau, *Chem. Rev.* **2011**, *111*, 1954–1993; l) C. S. Adams, C. D. Weatherly, E. G. Burke, J. M. Schomaker, *Chem. Soc. Rev.* **2014**, *43*, 3136–3163; m) M. A. Tius, *Chem. Soc. Rev.* **2014**, *43*, 2979–3002; n) S. Kitagaki, F. Inagaki, C. Mukai, *Chem. Soc. Rev.* **2014**, *43*, 2956–2978; o) Z. Wang, X. Xu, O. Kwon, *Chem. Soc. Rev.* **2014**, *43*, 2927–2940; p) T. Cañeque, F. M. Truscott, R. Rodriguez, G. Maestri, M. Malacria, *Chem. Soc. Rev.* **2014**, *43*, 2916–2926; q) J. Ye, S. Ma, *Acc. Chem. Res.* **2014**, *47*, 989–1000; r) J. Ye, S. Ma, *Org. Chem. Front.* **2014**, *1*, 1210–1224.

[10] a) R. Zeng, S. Wu, C. Fu, S. Ma, *J. Am. Chem. Soc.* **2013**, *135*, 18284 – 18287.
[11] F. Pan, C. Fu, S. Ma, *Chin. J. Org. Chem.* **2004**, *10*, 1168 – 1190.
[12] a) G. Zheng, Y. Li, J. Han, T. Xiong, Q. Zhang, *Nat. Commun.* **2015**, *6*, 7011, DOI: 10.1038/ncomms8011; b) H. Zhang, W. Pu, T. Xiong, Y. Li, X. Zhou, K. Sun, Q. Liu, Q. Zhang, *Angew. Chem. Int. Ed.* **2013**, *52*, 2529 – 2533; *Angew. Chem.* **2013**, *125*, 2589 – 2593; c) H. Zhang, Y. Song, J. Zhao, J. Zhang, Q. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 11079 – 11083; *Angew. Chem.* **2014**, *126*, 11259 – 11263.
[13] a) K. Kaneko, T. Yoshino, S. Matsunaga, M. Kanai, *Org. Lett.* **2013**, *15*, 2502 – 2505; b) B. Zhang, A. Studer, *Org. Lett.* **2014**, *16*, 1790 – 1793; for a palladium-catalyzed imidation of arenes with NFSI by a nitrogen radical pathway, see: c) G. B. Boursalian, M.-Y. Ngai, K. N. Hojczyk, T. Ritter, *J. Am. Chem. Soc.* **2013**, *135*, 13278 – 13281.
[14] A. I. O. Suarez, V. Lyaskovskyy, J. N. H. Reek, J. I. van der Vlugt, B. de Bruin, *Angew. Chem. Int. Ed.* **2013**, *52*, 12510 – 12529; *Angew. Chem.* **2013**, *125*, 12740 – 12760.
[15] Y.-J. Liu, H. Xu, W.-J. Kong, M. Shang, H.-X. Dai, J.-Q. Yu, *Nature* **2014**, *515*, 389 – 393.
[16] a) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881 – 1886; b) S. Purser, P. R. Moore, S. Swallow, V. Gouverneur, *Chem. Soc. Rev.* **2008**, *37*, 320 – 330; c) P. Jeschke, *ChemBioChem* **2004**, *5*, 570 – 589; d) S. M. Ametamey, M. Honer, P. A. Schubiger, *Chem. Rev.* **2008**, *108*, 1501 – 1516.
[17] K. K. J. Chan, D. O'Hagan, *Methods Enzymol.* **2012**, *516*, 219 – 235.
[18] For general reviews on the synthesis of organofluorine compounds, see: a) M. Shimizu, T. Hiyama, *Angew. Chem. Int. Ed.* **2005**, *44*, 214 – 231; *Angew. Chem.* **2005**, *117*, 218 – 234; b) "Flourishing Frontiers in Organofluorine Chemistry": *Organic Chemistry—Breakthroughs and Perspectives* (Eds.: K. Ding, L.-X. Dai) Wiley-VCH, Weiheim, **2012**; c) T. Liang, C. Neumann, T. Ritter, *Angew. Chem. Int. Ed.* **2013**, *52*, 8214 – 8264; *Angew. Chem.* **2013**, *125*, 8372 – 8423; d) M. G. Campbell, T. Ritter, *Chem. Rev.* **2015**, *115*, 612 – 633; e) P. A. Champagne, J. Desroches, J.-D. Hamel, M. Vandamme, J.-F. Paquin, *Chem. Rev.* **2015**, DOI: 10.1021/cr500706a.
[19] a) F. Yin, Z. Wang, Z. Li, C. Li, *J. Am. Chem. Soc.* **2012**, *134*, 10401 – 10404; b) C. Zhang, Z. Li, L. Zhu, L. Yu, Z. Wang, C. Li, *J. Am. Chem. Soc.* **2013**, *135*, 14082 – 14085; c) Z. Li, L. Song, C. Li, *J. Am. Chem. Soc.* **2013**, *135*, 4640 – 4643; d) Z. Li, Z. Wang, L. Zhu, X. Tan, C. Li, *J. Am. Chem. Soc.* **2014**, *136*, 16439 – 16443. For an intramolecular aminofluorination of activated allenes by a Ag^{II}-F reductive elimination mechanism, see: e) T. Xu, X. Mu, H. Peng, G. Liu, *Angew. Chem. Int. Ed.* **2011**, *50*, 8176 – 8179; *Angew. Chem.* **2011**, *123*, 8326 – 8329; f) For a palladium-catalyzed fluorination of arylboronic acid derivatives with selectfluor by fluorine-atom transfer, see: A. R. Mazzotti, M. G. Campbell, P. Tang, J. M. Murphy, T. Ritter, *J. Am. Chem. Soc.* **2013**, *135*, 14012 – 14015.
[20] C. L. Bumgardner, K. G. McDaniel, *J. Am. Chem. Soc.* **1969**, *91*, 1032 – 1034.
[21] A. B. Flynn, W. W. Ogilvie, *Chem. Rev.* **2007**, *107*, 4698 – 4745.
[22] See the Supporting Information for details.

Received: July 2, 2015
Revised: August 3, 2015
Published online: September 1, 2015

