JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Silver-Catalyzed Radical Aminofluorination of Unactivated Alkenes in Aqueous Media

Zhaodong Li, Liyan Song, and Chaozhong Li*

Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China

Supporting Information

ABSTRACT: We report herein a mild and catalytic intramolecular aminofluorination of unactivated alkenes. Thus, with the catalysis of $AgNO_3$, the reactions of various *N*-arylpent-4-enamides with Selectfluor reagent in CH_2Cl_2/H_2O led to the efficient synthesis of 5-fluoromethyl-substituted γ-lactams. A mechanism involving silver-catalyzed oxidative generation of amidyl radicals and silver-assisted fluorine atom transfer was proposed.

The introduction of fluorine atoms into organic molecules significantly changes their physical, chemical and biological properties, and thus, organofluorine compounds have found widespread and growing use in agrochemicals, pharmaceuticals, materials, and other industries.[1] Moreover, ^{18}F-labeled organic compounds are clinically used as contrast agents for positron emission tomography (PET).[2] The development of new methods for C−F bond formation under mild conditions has therefore received an increasing attention in the past four years.[3−11] In particular, free radical fluorination[7−11] is emerging as a powerful tool for C(sp^3)−F bond formation, especially under the catalysis of transition metals.[8−11] Lectka and co-workers[8] reported the copper-catalyzed aliphatic C−H fluorination with Selectfluor[12] (1-chloromethyl-4-fluorodiazoniabicyclo-[2,2,2]octane bis-(tetrafluoroborate)). Groves et al. successfully developed the manganese-catalyzed oxidative aliphatic C−H fluorination with fluoride ion.[9] We introduced the Ag(I)-catalyzed decarboxylative fluorination of aliphatic carboxylic acids with Selectfluor in aqueous solution.[10] In addition, Boger and Barker reported the Fe(III)/$NaBH_4$-mediated free radical hydrofluorination of unactivated alkenes.[11] It is certainly desirable to further explore the versatility and efficiency of radical fluorination. Herein, we report the Ag(I)-catalyzed radical aminofluorination[13,14] of unactivated alkenes in aqueous media.

Our idea was based on our recent finding[10] that the combination of Selectfluor and Ag(I) catalyst served not only as an oxidant, but also as a fluorine atom transfer agent in fluorodecarboxylation of aliphatic carboxylic acids, presumably via the intermediacies of Ag(III)F and Ag(II)F. We envisioned that such a combination might be utilized to allow the catalytic oxidative generation of amidyl radicals.[15,16] As depicted in Figure 1, *N*-arylpent-4-enamides (**1**) might be oxidized by the proposed intermediate Ag(III)F to generate Ag(II)F and arene radical cations **A**. The deprotonation of **A** gives amidyl radicals **B**, which then add intramolecularly to C=C double bonds in a 5-*exo* mode to afford carbon-centered radicals **C**. The

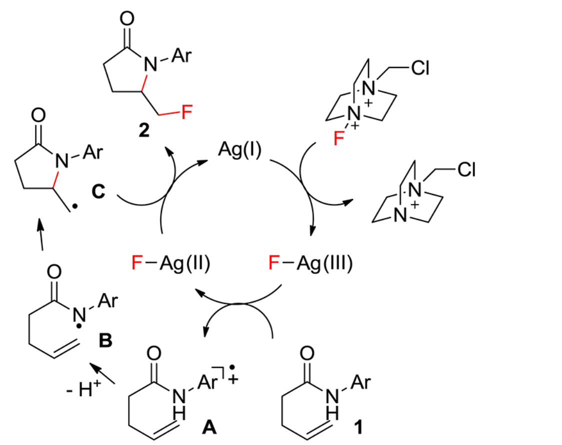


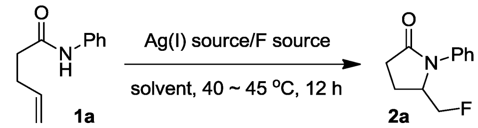
Figure 1. Proposed mechanism of radical aminofluorination of unactivated alkenes.

subsequent fluorine atom transfer from Ag(II)F to **C** produces the aminofluorination products **2** and regenerates Ag(I), which enters into the next catalytic circle. Driven by our interest in the reactivities of amidyl radicals[17] and in Ag(I)-catalyzed radical reactions,[10,18] we set out to explore this possibility.

Thus, *N*-phenylpent-4-enamide **1a** was chosen as the model substrate for the optimization of reaction conditions (Table 1). With 10 mol % $AgNO_3$ as the catalyst, the reaction of **1a** with Selectfluor (2 equiv) in organic solvents such as CH_3CN, DMF, acetone or CH_2Cl_2 at ambient temperature failed to give any desired product. However, when the aminofluorination was carried out in water at around 45 °C for 12 h, we were delighted to see that the expected lactam **2a** was observed in 76% yield. To improve the result, an organic cosolvent was used to increase the solubility of substrate **1a**. With CH_3CN or acetone as the cosolvent, the reaction was somehow complicated and no **2a** could be detected. On the other hand, the use of CH_2Cl_2 as the cosolvent led to a higher yield of **2a** (91% yield). Benzene showed a behavior similar to CH_2Cl_2. These different solvent effects might be rationalized by the fact that the biphasic system (such as CH_2Cl_2/H_2O) keeps the product from further oxidation. In this respect, increasing the ratio of CH_2Cl_2/H_2O from 1:1 to 2:1 helped for most substrates (vide infra), although no difference was observed for **1a**. Reducing the amount of $AgNO_3$ slowed down the aminofluorination while no expected product could be detected without $AgNO_3$. Changing $AgNO_3$ to AgOAc or AgOTf did

Received: January 5, 2013
Published: March 18, 2013

Table 1. Optimization of Reaction Conditions



en-try[a]	catalyst (mol %)	F source	solvent	yield (%)[b]
1	$AgNO_3$ (10)	Selectfluor	CH_2Cl_2, CH_3CN, Me_2CO or DMF	0
2	$AgNO_3$ (10)	Selectfluor	H_2O	76
3	$AgNO_3$ (10)	Selectfluor	CH_3CN/H_2O[c]	0
4	$AgNO_3$ (10)	Selectfluor	CH_2Cl_2/H_2O[c]	91
5	$AgNO_3$ (10)	Selectfluor	PhH/H_2O[c]	86
6	AgNO3 (5)	Selectfluor	CH_2Cl_2/H_2O[c]	65
7	none	Selectfluor	CH_2Cl_2/H_2O[c]	0
8	AgOAc (10)	Selectfluor	CH_2Cl_2/H_2O[c]	89
9	AgOTf (10)	Selectfluor	CH_2Cl_2/H_2O[c]	90
10	$AgNO_3$ (10)	NFSI	CH_2Cl_2/H_2O[c]	0

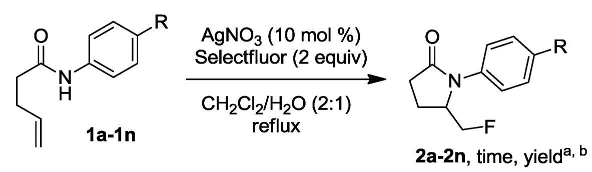
[a]Conditions: **1a** (0.3 mmol), fluorine source (0.6 mmol), organic solvent (3 mL) if applied, H_2O (3 mL) if applied, Ag source, 40–45 °C, 12 h. [b]Isolated yield based on **1a**. [c]The ratio is 1:1 (v:v).

not show much difference. However, no reaction occurred when the fluorine source was switched to *N*-fluorobis-(benzenesulfonyl)imide (NFSI).

With the optimized conditions in hand, we then explored the scope and limitations of the above radical aminofluorination, and the results are summarized in Schemes 1 and 2. The *para*-substituent effect was first examined (Scheme 1). The aminofluorination proceeded smoothly not only for the *N*-arylamides bearing an electron-donating group on the aryl ring (**1b**−**1e**), but also for those substrates having a strong electron-withdrawing substituent (**2g**−**2m**) such as CN, NO_2, CF_3, CO_2H, although a longer reaction time was required in the latter cases. Nevertheless, *N*-(*p*-methoxyphenyl)-amide **1n** failed to give the desired product **2n**. Instead, the formation of benzoquinone was observed in about 30% yield. Presumably the oxidation of **1n** to radical cations **A** was followed by nucleophilic attack (by water) rather than deprotonation (to give amidyl radicals **B**), a procedure similar to CAN (cerium ammonium nitrate)-mediated deprotection of *N*-(*p*-methoxyphenyl)-protected amides.[19] In the meantime, primary or *N*-alkyl-substituted amides did not undergo aminofluorination under the optimized conditions. These results were in accordance with the proposed mechanism illustrated in Figure 1.[20] The above results also demonstrated the excellent functional group compatibility of the radical aminofluorination.

Next, substrates **3a**−**3q** with various substitution patterns were screened (Scheme 2). The reactions of *meta*- or *ortho*-substituted aromatic amides (**3a**−**3g**) all proceeded nicely. Substrates with different substitution on the alkenyl chain also underwent smooth 5-*exo* cyclization. Di- and trisubstituted alkenes (such as **3j**, **3l** and **3m**) were also applicable for the aminofluorination. Other than amides, *N*-arylcarbamates and

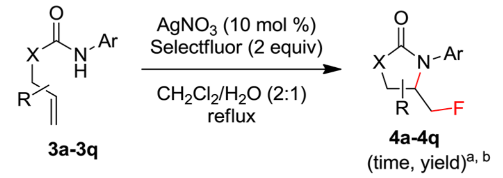
Scheme 1. *para*-Substituent Effect in the Aminofluorination of *N*-Arylpent-4-enamides[a,b,c]

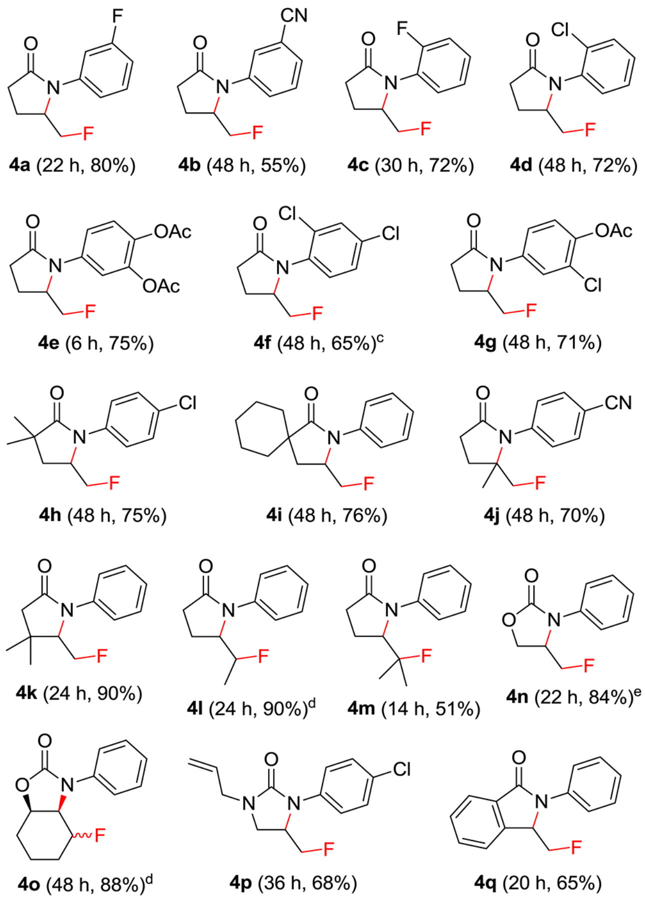


2a (R = H),	12 h,	91%	**2h** (R = CF_3),	48 h,	73%
2b (R = *t*-Bu)[c],	36 h,	85%	**2i** (R = Ac),	24 h,	75%
2c (R = OAc),	6 h,	91%	**2j** (R = CO_2Et),	36 h,	83%
2d (R = OCF_3),	6 h,	86%	**2k** (R = CO_2H),	48 h,	55%
2e (R = NPhth)[c],	12 h,	63%	**2l** (R = CN),	48 h,	75%
2f (R = Cl)[c],	16 h,	85%	**2m** (R = NO_2),	48 h,	50%
2g (R = F),	22 h,	83%	**2n** (R = OMe),	12 h,	0%

[a]Reaction conditions: alkene (0.3 mmol), $AgNO_3$ (0.03 mmol), Selectfluor (0.6 mmol), CH_2Cl_2 (1.5 mL), H_2O (0.75 mL), reflux. [b]Isolated yield based on the starting alkene. [c]CH_2Cl_2 (3 mL) and H_2O (3 mL) was used as the solvent.

Scheme 2. Silver-Catalyzed Aminofluorination of Unactivated Alkenes[a,b,c,d,e]

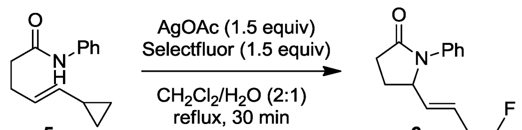




[a,b]See Scheme 1. [c]Thirty mole percent $AgNO_3$ was used. [d]Two stereoisomers in 1:1 ratio. [e]CH_2Cl_2 (3 mL) and H_2O (3 mL) was used as the solvent.

ureas could also be utilized to participate in the transformation, as exemplified by the synthesis of **4n**−**4p** from the corresponding substrates **3n**−**3p**. It is conceivable that the hydrolysis of **4n**−**4p** would produce the corresponding fluorinated 1,2-diamines or aminoalcohols, which should serve as useful building blocks in the synthesis of fluorinated molecules.

To provide further evidence on the proposed radical mechanism (Figure 1), (*E*)-5-cyclopropyl-*N*-phenylpent-4-enamide (**5**) was prepared as the radical probe.[21] The reaction of **5** under the above optimized conditions turned out to be unsatisfactory probably because of the instability of the expected allylic amine product **6** under the oxidative conditions. However, by using 1.5 equiv of AgOAc and shortening the reaction time to 30 min, the ring-opening product **6** of (*E*)-configuration was isolated in 23% yield along with the recovery of **5** in 30% yield (eq 1). This experiment provides a solid

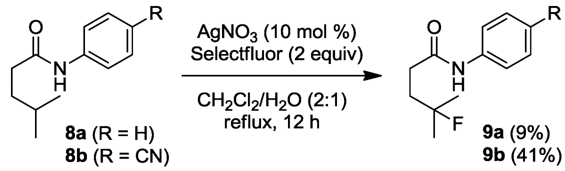


5 **6** (1)

evidence for the intermediacy of amidyl radicals in the aminofluorination. Moreover, treatment of amide **1a** with $AgNO_3$ (20 mol %), $K_2S_2O_8$ (2 equiv) and KF (2 equiv) in CH_2Cl_2/H_2O at reflux for 12 h led to the formation of 5-methyl-1-phenylpyrrolidin-5-one (**7**, 23% yield) rather than **2a**. Apparently **7** resulted from the H-abstraction of cyclized radical **C**. This implies that the H-abstraction is much faster than the further oxidation for radical **C**. The reaction of **1a** with $Ag(Phen)_2S_2O_8$ (2 equiv) and Selectfluor (2 equiv) in CH_2Cl_2/H_2O or CH_3CN/H_2O at refluxing temperature gave not **2a** but **7** (10−30%) as the product, indicating that **2a** is unlikely to be formed via the direct trapping of radical **C** by Selectfluor. These results, in combination with our previous finding in decarboxylative fluorination,[10] support the silver-assisted fluorine atom transfer mechanism.

The above radical aminofluorination of unactivated alkenes exhibits the behavior different from the reported palladium-catalyzed processes, in which N-tosyl or N-nosyl-substituted 3-fluoropiperidines was obtained via a 6-*endo* mode of cyclization and the procedure was not applicable to amides.[13a] Other reported nonradical aminofluorination processes also gave *endo*-cyclization products.[13c−e] It is worth mentioning that electrophilic halocyclizations[22] of unsaturated amides typically afford lactones or oxazolines[6a] rather than lactams. In addition, the fact that amidyl radicals can be accessed directly from the parent amides under silver catalysis should be valuable for the design of a range of other reactions.[15,16,23]

As an extension of the above aminofluorination, the following remote C−H fluorination could be designed based on the intramolecular 1,5-H abstraction of amidyl radicals.[23l] Our preliminary results showed that, under the conditions identical to those of aminofluorination detailed above, the reaction of 4-methyl-*N*-phenylpentanamide (**8a**) afforded the fluorinated product **9a** in 9% yield. However, with *para*-cyano-substituted aromatic amide **8b** as the substrate, the corresponding fluorinated product **9b** was achieved in 41% yield (eq 2). The *para*-cyano-substitution effect might be attributed to the higher N−H bond dissociation energy in **8b** than in **8a**, which serves as a better driving force for 1,5-H



8a (R = H) **8b** (R = CN) **9a** (9%) **9b** (41%) (2)

migration. These results provide a promising route for site-specific C−H fluorination, which is currently under further investigation in our laboratory.

In conclusion, we have developed the radical amino-fluorination of unactivated alkenes in aqueous media with $AgNO_3$ as the catalyst and Selectfluor as both the fluorine source and the oxidant. This new method further broadens the scope of radical fluorination and features (1) the catalytic oxidative generation of amidyl radicals and (2) the silver-assisted fluorine atom transfer. In view of the mild conditions and excellent functional group compatibility, this radical procedure should find practical application in the synthesis of fluorinated molecules.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details, characterizations of new compounds, and copies of ^1H, ^{13}C and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

clig@mail.sioc.ac.cn

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation of China (Grant nos. 21072211, 21228202, 21272259 and 21290180) and by the National Basic Research Program of China (973 Program) (Grant nos. 2011CB710805 and 2010CB833206).

■ REFERENCES

(1) (a) Müller, K.; Faeh, C.; Diederich, F. *Science* **2007**, *317*, 1881. (b) O'Hagan, D. *Chem. Soc. Rev.* **2008**, *37*, 308. (c) Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. *Chem. Soc. Rev.* **2008**, *37*, 320. (d) Kirk, K. L. *Org. Process Res. Dev.* **2008**, *12*, 305.

(2) Miller, P. W.; Long, N. J.; Vilar, R.; Gee, A. D. *Angew. Chem., Int. Ed.* **2008**, *47*, 8998.

(3) Furuya, T.; Kuttruff, C. A.; Ritter, T. *Curr. Opin. Drug Discovery Dev.* **2008**, *11*, 803.

(4) For the latest selected reviews, see: (a) Grushin, V. V. *Acc. Chem. Res.* **2010**, *43*, 160. (b) Furuya, T.; Klein, J. E. M. N.; Ritter, T. *Synthesis* **2010**, *42*, 1804. (c) Furuya, T.; Kamlet, A. S.; Ritter, T. *Nature* **2011**, *473*, 470.

(5) For the latest selected examples of $C(sp^2)$−F bond formations, see: (a) Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; García-Fortanet, J.; Kinzel, T.; Buchwald, S. L. *Science* **2009**, *325*, 1661. (b) Tang, P.; Furuya, T.; Ritter, T. *J. Am. Chem. Soc.* **2010**, *132*, 12150. (c) Lee, E.; Kamlet, A. S.; Powers, D. C.; Neumann, C. N.; Boursalian, G. B.; Furuya, T.; Choi, D. C.; Hooker, J. M.; Ritter, T. *Science* **2011**, *334*, 639.

(6) For the latest selected examples of $C(sp^3)$−F bond formations via nonradical mechanisms, see: (a) Rauniyar, V.; Lackner, A. D.; Hamilton, G. L.; Toste, F. D. *Science* **2011**, *334*, 1681. (b) Mankad, N. P.; Toste, F. D. *Chem. Sci.* **2012**, *3*, 72.

(7) (a) Rueda-Becerril, M.; Sazepin, C. C.; Leung, J. C. T.; Okbinoglu, T.; Kennepohl, P.; Paquin, J.-F.; Sammis, G. M. *J. Am. Chem. Soc.* **2012**, *134*, 4026. (b) Leung, J. C. T.; Chatalova-Sazepin, C.; West, J. G.; Rueda-Becerril, M.; Paquin, J.-F.; Sammis, G. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 10804.
(8) Bloom, S.; Pitts, C. R.; Miller, D. C.; Haselton, N.; Holl, M. G.; Urheim, E.; Lectka, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 10580.
(9) Liu, W.; Huang, X.; Cheng, M.-J.; Nielsen, R. J.; Goddard, W. A., III; Groves, J. T. *Science* **2012**, *337*, 1322.
(10) Yin, F.; Wang, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 10401.
(11) Barker, T. J.; Boger, D. L. *J. Am. Chem. Soc.* **2012**, *134*, 13588.
(12) (a) Singh, R. P.; Shreeve, J. M. *Acc. Chem. Res.* **2004**, *37*, 31. (b) Nyffeler, P. T.; Durón, S. G.; Burkart, M. D.; Vincent, S. P.; Wong, C.-H. *Angew. Chem., Int. Ed.* **2005**, *44*, 192.
(13) For nonradical aminofluorination of alkenes, see: (a) Wu, T.; Yin, G.; Liu, G. *J. Am. Chem. Soc.* **2009**, *131*, 16354. (b) Qiu, S.; Xu, T.; Zhou, J.; Guo, Y.; Liu, G. *J. Am. Chem. Soc.* **2010**, *132*, 2856. (c) Lozano, O.; Blessley, G.; del Campo, T. M.; Thompson, A. L.; Giuffredi, G. T.; Bettati, M.; Walker, M.; Borman, R.; Gouverneur, V. *Angew. Chem., Int. Ed.* **2011**, *50*, 8105. (d) Wang, Q.; Zhong, W.; Wei, X.; Ning, M.; Meng, X.; Li, Z. *Org. Biomol. Chem.* **2012**, *10*, 8566. (e) Kong, W.; Feige, P.; de Haro, T.; Nevado, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 2469. (f) Yadav, J. S.; Reddy, B. V. S.; Chary, D. N.; Chandrakanth, D. *Tetrahedron Lett.* **2009**, *50*, 1136. (g) Appayee, C.; Brenner-Moyer, S. E. *Org. Lett.* **2010**, *12*, 3356.
(14) For nonradical aminofluorination of activated allenes and alkynes, see: (a) Mu, X.; Wu, T.; Peng, H.; Liu, G. *Angew. Chem., Int. Ed.* **2011**, *50*, 8176. (b) Xu, T.; Liu, G. *Org. Lett.* **2012**, *14*, 5416.
(15) For reviews on amidyl radicals, see: (a) Stella, L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 337. (b) Esker, J. L.; Newcomb, M. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1993; Vol. *58*, pp 1−45. (c) Zard, S. Z. *Synlett* **1996**, *7*, 1148. (d) Fallis, A. G.; Brinza, I. M. *Tetrahedron* **1997**, *53*, 17543. (e) Stella, L. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. *2*, pp 407−424. (f) Zard, S. Z. *Chem. Soc. Rev.* **2008**, *37*, 1603. (g) Baralle, A.; Baroudi, A.; Daniel, M.; Fensterbank, L.; Goddard, J.-P.; Lacote, E.; Larraufie, M.-H.; Maestri, G.; Malacria, M.; Ollivier, C. In *Encyclopedia of Radicals in Chemistry, Biology and Materials*; Chatgilialoglu, C., Studer, A., Eds.; Wiley: Chichester, U.K., 2012; pp 767−816.
(16) For the *o*-iodoxybenzoic acid (IBX)-mediated oxidative generation of amidyl radicals, see: (a) Nicolaou, K. C.; Baran, P. S.; Zhong, Y.-L.; Choi, H.-S.; Yoon, W. H.; He, Y.; Fong, K. C. *Angew. Chem., Int. Ed.* **1999**, *38*, 1669. (b) Nicolaou, K. C.; Zhong, Y.-L.; Baran, P. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 625. (c) Nicolaou, K. C.; Baran, P. S.; Kranich, R.; Zhong, Y.-L.; Sugita, K.; Zou, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 202. (d) Nicolaou, K. C.; Baran, P. S.; Zhong, Y.-L.; Barluenga, S.; Hunt, K. W.; Kranich, R.; Vega, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 2233. (e) Janza, B.; Studer, A. *J. Org. Chem.* **2005**, *70*, 6991.
(17) (a) Tang, Y.; Li, C. *Org. Lett.* **2004**, *6*, 3229. (b) Lu, H.; Li, C. *Tetrahedron Lett.* **2005**, *46*, 5983. (c) Chen, Q.; Shen, M.; Tang, Y.; Li, C. *Org. Lett.* **2005**, *7*, 1625. (d) Hu, T.; Shen, M.; Chen, Q.; Li, C. *Org. Lett.* **2006**, *8*, 2647. (e) Yuan, X.; Liu, K.; Li, C. *J. Org. Chem.* **2008**, *73*, 6166. (f) Zhuang, S.; Liu, K.; Li, C. *J. Org. Chem.* **2011**, *76*, 8100.
(18) (a) Wang, Z.; Zhu, L.; Yin, F.; Su, Z.; Li, Z.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 4258. (b) Liu, X.; Wang, Z.; Cheng, X.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 14330.
(19) Kronenthal, D. R.; Han, C. Y.; Taylor, M. K. *J. Org. Chem.* **1982**, *47*, 2765.
(20) An alternative mechanism for the aminofluorination is the N-fluorination of the unsaturated amides followed by the fluorine atom transfer cyclization. However, the failure of primary and *N*-alkyl amides in aminofluorination seems to discourage this hypothesis.
(21) Newcomb, M. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M. P., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. *1*, pp 317−336.
(22) For selected reviews, see: (a) Robin, S.; Rousseau, G. *Tetrahedron* **1998**, *54*, 13681. (b) Robin, S.; Rousseau, G. *Eur. J. Org. Chem.* **2002**, *2002*, 3099.
(23) Amidyl radicals are typically generated via the homocleavage of weak N−heteroatom (S, O, N, halogen, etc.) bonds. For representative examples, see: (a) Lyaskovskyy, V.; Suarez, A. I. O.; Lu, H.; Jiang, H.; Zhang, X. P.; de Bruin, B. *J. Am. Chem. Soc.* **2011**, *133*, 12264. (b) Guin, J.; Fröhlich, R.; Studer, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 779. (c) Guin, J.; Mück-Lichtenfeld, C.; Grimme, S.; Studer, A. *J. Am. Chem. Soc.* **2007**, *129*, 4498. (d) Kemper, J.; Studer, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 4914. (e) Klugge, J.; Herdtweck, E.; Bach, T. *Synlett* **2004**, *15*, 1199. (f) Moutrille, C.; Zard, S. Z. *Chem. Commun.* **2004**, *40*, 1848. (g) Gagosz, F.; Moutrille, C.; Zard, S. Z. *Org. Lett.* **2002**, *4*, 2707. (h) Cassayre, J.; Gagosz, F.; Zard, S. Z. *Angew. Chem., Int. Ed.* **2002**, *41*, 1873. (i) Artman, G. D., III; Waldman, J. H.; Weinreb, S. M. *Synlett* **2002**, *13*, 2057. (j) Esker, J. K.; Newcomb, M. *Tetrahedron Lett.* **1993**, *34*, 6877. (k) Concepcion, J. I.; Francisco, C. G.; Hernandez, R.; Salazar, J. A.; Suarez, E. *Tetrahedron Lett.* **1984**, *25*, 1953. (l) Barton, D. H. R.; Beckwith, A. L. J.; Goosen, A. *J. Chem. Soc.* **1965**, 181.