Carbenes

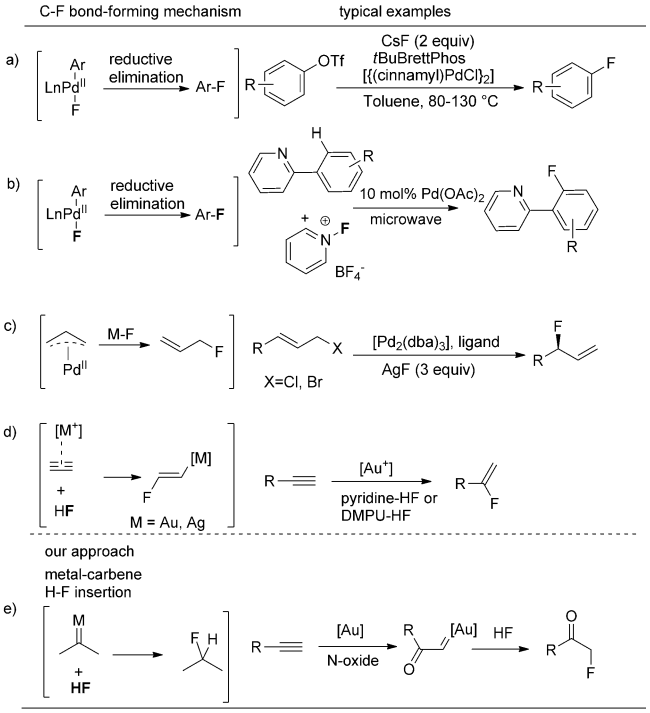
International Edition: DOI: 10.1002/anie.201603914
German Edition: DOI: 10.1002/ange.201603914

Synthesis of α-Fluoroketones by Insertion of HF into a Gold Carbene

*Xiaojun Zeng, Shiwen Liu, Zhenyu Shi, Guangchang Liu, and Bo Xu**

Abstract: *Reported is an efficient synthesis of α-fluoroketones by insertion of hydrogen fluoride (HF) into the gold carbene intermediate, generated from a cationic gold catalyzed addition of N-oxides to alkynes. This method results in excellent chemical yields for a wide range of alkyne substrates and demonstrates good functional-group tolerance.*

Fluorine substitution is a proven and successful strategy in pharmaceuticals, agrochemicals, and materials research.[1] However, introducing fluorine into organic molecules has been a long-standing challenge for organic chemists.[1j] In recent years, more and more attention has been paid to transition metal catalyzed fluorinations.[2] But fluorine is not a transition metal friendly element, and well-defined transition metal catalyzed C–F bond-formation processes with broad scope are surprisingly rare (Scheme 1).[2b] One important process is reductive elimination from either R-Pd^{II}-F (Scheme 1 a)[3] or R-Pd^{IV}-F (Scheme 1 b).[4] Another C–F bonding-forming mechanism is the attack of a nucleophilic fluorine source to an allyl palladium complex (Tsuji–Trost-type reaction; Scheme 1 c).[5] C–F bond formation can also be achieved through addition of HF to alkynes activated by cationic metals (e.g. Au, Ag; Scheme 1 d).[6] This process has been used in gold-catalyzed hydrofluorination of alkynes by the group of Sadighi[7] as well as ourseleves.[8] In addition, other mechanisms like silver-based reductive elimination,[9] fluorodemetalation,[10] fluoropalladium,[11] and aminofluorination[12] have been proposed, although these mechanisms are not well defined.



Scheme 1. Common C–F bond-formation mechanisms in transition-metal catalysis. BrettPhos = 2-(dicyclohexylphosphino)-3,6-dimethoxy-2′,4′,6′-triisopropyl-1,1′-biphenyl, dba = dibenzylideneacetone, DMPU = 1,3-dimethy1-2-oxohexahydropyri midine.

Transition metal mediated C–F bond formations are almost always much more difficult than their nonfluorine counterparts (e.g. C–C, C–O bond formations).[13] In general, they have narrower scope and often need special ligands/reagents and harsh reaction conditions, such as strong oxidants and high temperature. Because of limitations of existing C–F bond-forming pathways, it is highly desirable to find a new, efficient, and broadly applicable C–F bond-forming strategy. Our strategy for transition metal catalyzed fluorination moves away from these processes, and employs another elementary process, that is, insertion HF into metal carbene intermediates (Scheme 1 e). Although fluorination of carbene precursors, like diazo compounds, has been reported,[14] as far as we know, HF insertion into a metal carbene intermediate has not been used in transition metal catalyzed fluorinations.

Our proof of concept application was difunctionalization of alkynes to give α-fluoroketones (Scheme 1 e). The method we used to generate the gold carbene[15] is the gold-catalyzed alkyne oxidation by *N*-oxides, a protocol developed by the groups of Zhang[16] and others.[17] *N*-oxide is a mild oxidant, so this fluorination protocol is expected to have good functional-group tolerance.

α-Fluoroketones are important building blocks and motifs in medicinal chemistry.[18] One straightforward method for the synthesis of α-fluoroketones is electrophilic fluorination of the corresponding ketones or nucleophilic fluorine displacement of α-haloketones,[1j] but this method has an inherent regioselectivity problem. The groups of Nevado[19] and Gouverneur,[20] as well as ours[21] have developed the synthesis of α-fluoroketones by gold-catalyzed fluorinations of alkynes. Yang and co-workers have reported a synthesis of α-fluoroketones through oxidation of aromatic alkenes by a radical mechanism.[22] All these methods are based on the electrophilic fluorination reagent Selectfluor, which is a strong oxidant, especially when used with transition-metal catalysts. As a result, these methods have limited scope as

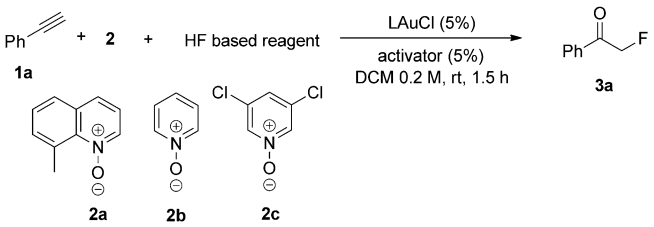
[*] X. Zeng, S. Liu, Z. Shi, G. Liu, Dr. B. Xu
College of Chemistry, Chemical Engineering and Biotechnology
Donghua University
2999 North Renmin Lu, Shanghai 201620 (China)
E-mail: bo.xu@dhu.edu.cn

Supporting information for this article can be found under: http://dx.doi.org/10.1002/anie.201603914.

most of substrates are either simple unfunctionalized alkynes or alkenes.

We used the fluorination of the alkyne **1a** as our model reaction to study the HF insertion protocol (Table 1). We used

Table 1: Development of reaction conditions.[a]



Entry	[Au]	Activator	2	HF Reagent	Yield [%][b]
1	PPh_3AuCl	AgOTf	**2a**	Pyridine-HF	trace
2	PPh_3AuCl	$AgNTf_2$	**2a**	Pyridine-HF	70%
3	PPh_3AuCl	$AgSbF_6$	**2a**	Pyridine-HF	trace
4	PPh_3AuCl	NaBARF	**2a**	Pyridine-HF	trace
5	PPh_3AuCl	AgOTs	**2a**	Pyridine-HF	trace
6	$(RO)_3PAuCl$[c]	$AgNTf_2$	**2a**	Pyridine-HF	44
7	*t*BuXPhosAuCl	$AgNTf_2$	**2a**	Pyridine-HF	54
8	XPhos	$AgNTf_2$	**2a**	Pyridine-HF	77
9	JohnPhos-AuCl	$AgNTf_2$	**2a**	Pyridine-HF	89
10	SPhos-Au-Cl	$AgNTf_2$	**2a**	Pyridine-HF	85
11	$Dppf(AuCl)_2$	$AgNTf_2$	**2a**	Pyridine-HF	trace
12	JohnPhos-AuCl	$AgNTf_2$	**2b**	Pyridine-HF	n.r.
13	JohnPhos-AuCl	$AgNTf_2$	**2c**	Pyridine-HF	n.r.
14	JohnPhos-AuCl	$AgNTf_2$	**2a**	Et_3N-HF	n.r.
15	JohnPhos-Au-NTf_2 (0.5% loading)	–	**2a**	Pyridine-HF	90[d]

[a] Reaction conditions: **1a** (0.2 mmol), *N*-oxide **2** (0.28 mmol), pyridine-HF (1.3 mmol HF, 6.5 equiv), ligand-AuCl (5 mol%), and activator (5 mol%) were stirred in DCM (1 mL) at RT in a sealed polypropylene tube for 1.5 h. [b] Determined by GC-MS analysis. [c] $R = 2,4\text{-di-}t\text{Bu}C_6H_3$. [d] Reaction time 24 h. DCM = dichloromethane, Dppf = 1,1′-bis(diphenylphosphanyl)ferrocene, JohnPhos = 2-dicyclohexylphosphinobiphenyl, SPhos = 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl, XPhos = 2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl, Tf = trifluoromethanesulfonyl.

8-methylquinoline *N*-oxide (**2a**) as our oxidant and pyridine-HF as our fluorine source. First, screening of silver activators indicated $AgNTf_2$ was the best choice (entries 1–5). Then we investigated the ligand effects (entries 6–11).[23] In general, gold catalysts derived from Buchwald-type ligands gave good results, and among them the JohnPhos-based gold catalyst gave the best chemical yield (entry 9). It was interesting to see that the bidentate-ligand-based (Dppf) gold catalyst only gave trace product (entry 11). Other *N*-oxides such as pyridine *N*-oxide (**2b**) and dichloropyridine *N*-oxide (**2c**) could not mediate this reaction (entries 12 and 13). We also tested another HF-based fluorination reagent Et_3N-HF, but no reaction took place (entry 14). The low reactivity of the Et_3N-HF system may be due to high basicity of Et_3N.[8] Previously, we found that excess amounts of silver activators are harmful to gold-catalyzed reactions, and preformed cationic gold catalysts usually have the best efficiency.[24] Indeed, the preformed gold catalyst JohnPhos-Au-NTf_2 gave a faster reaction, and we could even reduce the gold catalyst loading to 0.5 mol%, although longer reaction time was needed (entry 15). It should be noted this reaction is not sensitive to moisture and oxygen as the reactions can be conducted at ambient atmosphere without any precautions.

With the optimized reaction conditions in hand, we explored the scope and functional-group tolerance of our HF insertion protocol (Table 2). First we evaluated aromatic terminal alkynes (**3a–u**). Phenyl acetylene and alkyl-group-substituted phenyl acetylenes all gave excellent yields of α-fluoroketones (**3a–c**). Electron-rich phenol and phenol ether groups were also well tolerated (**3d–g**), and this kind of functional-group tolerance is not possible when strong oxidants like Selectfluor are used.[25] Electron-withdrawing functional-groups (ketone, ester, and acetonitrile) on the aryl group of the alkynes all gave excellent yields (**3h–j**). Nonbasic amine groups (TsNH, TsMeN) are also well tolerated (**3k**,**l**). Halogen-substituted (F, Cl, Br) phenyl acetylenes all gave excellent yields of the products **3**. In general, substitution patterns (*ortho*, *meta*, *para*) and the presence of either electron-donating or electron-withdrawing groups on the aromatic ring of alkynes have little influence on the efficiency of the reactions.

We also tested alkynes containing fused aromatics and heteroaromatics (naphthalene, thiophene, benzothiophene, indole, benzofuran), and they all gave excellent results (Table 2, **3q–u**). It should be noted that these heteroaromatics are highly electron rich and can be easily oxidized, but they all tolerated our reaction conditions. An alkenyl-substituted alkyne (enyne) also worked well, and the highly functionalized fluoroketone **3v** was obtained in good yield.

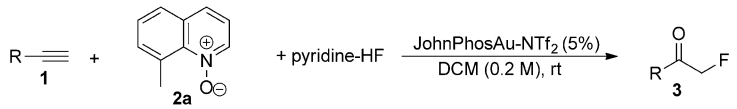
We then moved our focus to reactions of aliphatic alkynes. Simple unfunctionalized aliphatic alkynes worked very well (Table 2, **3w–y**). And various common functional groups (allyl, ether, ester, halogen, tosylate, mesylate, amide) are well tolerated (**3z-ah**), and in all cases excellent yields of the products **3** were obtained. Finally, we explored the feasibility of our method in synthesis of complex target molecules. We were glad to find that a structurally complex and highly biologically important glycoside, an estrone derivative, and a cholesterol derivative were suitable substrates and excellent product yields (**3ai–ak**) were obtained.

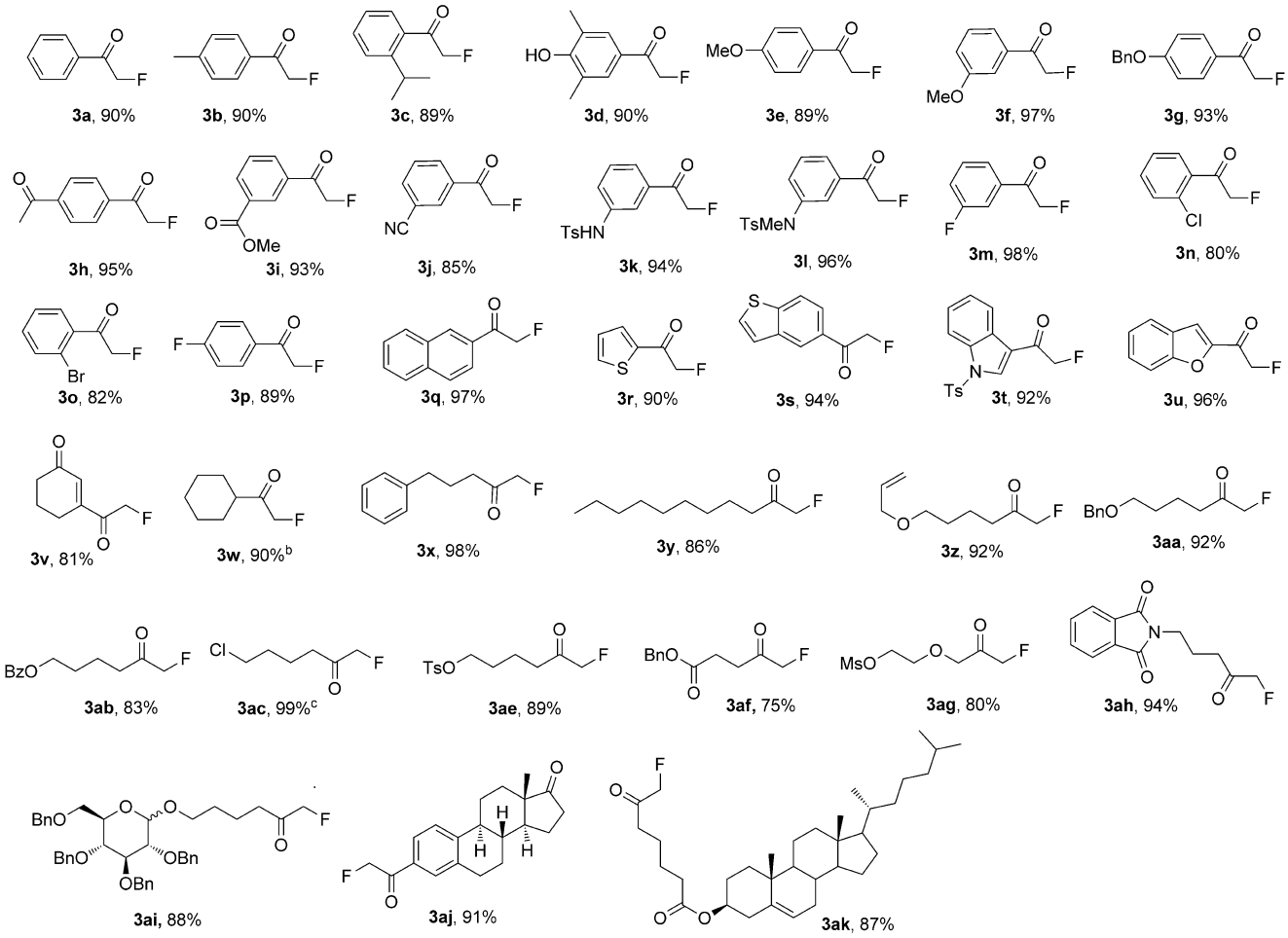
In general, our method did not work for internal alkynes (sluggish reaction). Because of the lower reactivity of internal alkynes, the generation of a gold carbene is very slow.[16a–e] For alkynes with strong nucleophilic groups present (e.g. propargyl alcohol), our method did not give a clean transformation, and it could be due to the nucleophilic groups competing with the *N*-oxide in the addition to the alkyne.

The α-fluoroketones **3** are versatile building blocks in synthesis (Scheme 2). It can be simply reduced by $NaBH_4$ to give the fluorohydrin **4** in quantitative yield.[26] **3** can also react with aldehyde to give the aldol condensation product **5** (fluorinated α,β-unsaturated ketone).[27] Reaction of **3** with a Michael acceptor gives the 1,4-addition product **6** via an enamine intermediate.[28] And reductive amination of **3** gives the β-fluoroamine **7** in good yield.[29]

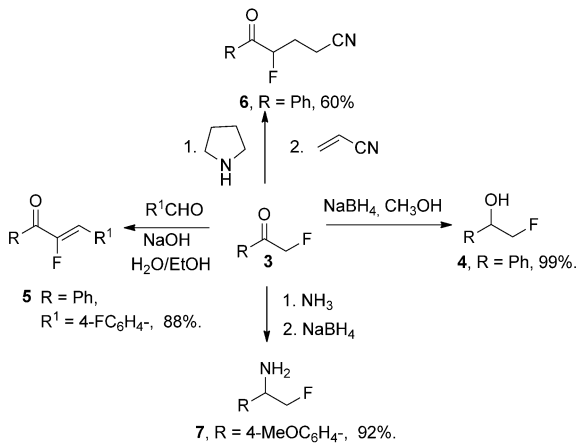
Our proposed mechanism is shown in Scheme 3. Our preferred mechanism is the carbene pathway, the key step of

Table 2: Scope for the synthesis of α-fluoroketones **3**.[a]

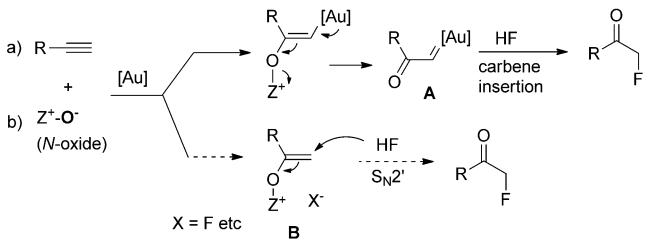




[a] Reaction conditions: alkyne **1** (0.2 mmol), *N*-oxide **2a** (0.28 mmol), pyridine-HF (1.3 mmol), and JohnPhosAuNTf$_2$ (5 mol%) in DCM (1 mL) at RT. All yields are those of the isolated products unless otherwise stated. [b] Determined by GC-MS analysis. [c] Determined by ^{1}H NMR spectroscopy. Ts = 4-toluenesulfonyl.



Scheme 2. Synthetic applications of the α-fluoroketones **3**.



Scheme 3. Proposed mechanism.

which is the insertion of HF into the gold carbene intermediate **A** (Scheme 3a). Zhang and co-workers recently reported that an alkyne could react with *N*-oxide to give the pyridinium enolate salt **B** in the presence of stoichiometric amount of HNTf$_2$. **B** could react with a nucleophile by a S_N2'

pathway,[30] and serves as an alternative pathway for the formation of fluoroketones (Scheme 3b). We think this pathway is unlikely. First, the generation of **B** needs a strong acid ($HNTf_2$)[30] and pyridine-HF is only weakly acidic, and we did not detect formation of **B** during the course of the reaction. Second, the reactivity of **B** is relatively low,[30] and in our fluorination protocol, many reactions could complete at room temperature in less than 5 minutes. This high reactivity can only be explained by the intermediacy of the highly reactive **A**.

In summary, our new synthesis of α-fluoroketones by insertion of HF into a gold carbene intermediate is a practical efficient method. Most functional groups can be tolerated and the reactions can be conducted at ambient atmosphere without any precautions. Because only a mild oxidant, *N*-oxide, is used, compared to literature methods, it has high functional-group tolerance. Other fluorination systems based on the insertion of HF into gold carbenes are currently being investigated in our laboratory and will be communicated in due course.

Acknowledgements

We are grateful to the National Science Foundation of China (NSFC-21472018) and China Recruitment Program of Global Experts for financial support. We are also thankful to Prof. Zhijia Zhu for his support with the NMR experiments. X. Zeng is grateful to Prof. Jing Xu (SUSTC) for his support and encouragement.

Keywords: carbenes · fluorine · gold · nitrogen oxides · reaction mechanisms

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 10032–10036
Angew. Chem. **2016**, *128*, 10186–10190

[1] a) R. D. Chambers, *Fluorine in organic chemistry*, Blackwell/CRC, Boca Raton, **2004**; b) T. Hiyama, *Organofluorine compounds, chemistry and applications*, Springer, Berlin, **2000**; c) P. Kirsch, *Modern fluoroorganic chemistry*, Wiley-VCH, Weinheim, **2004**; d) K. Muller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; e) M. Schlosser, *Angew. Chem. Int. Ed.* **1998**, *37*, 1496; *Angew. Chem.* **1998**, *110*, 1538; f) V. A. Soloshonok, *Fluorine-containing synthons, ACS symposium series 911*, Oxford University Press, Washington, DC, **2005**; g) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, **2006**; h) G. Gerebtzoff, X. Li-Blatter, H. Fischer, A. Frentzel, A. Seelig, *ChemBioChem* **2004**, *5*, 676–684; i) K. Müller, C. Faeh, F. Diederich, *Science* **2007**, *317*, 1881–1886; j) P. A. Champagne, J. Desroches, J.-D. Hamel, M. Vandamme, J.-F. Paquin, *Chem. Rev.* **2015**, *115*, 9073–9174.

[2] a) V. Gouverneur, *Science* **2009**, *325*, 1630–1631; b) Z. Jin, G. B. Hammond, B. Xu, *Aldrichimica Acta* **2012**, *45*, 67–83.

[3] a) D. A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. García-Fortanet, T. Kinzel, S. L. Buchwald, *Science* **2009**, *325*, 1661–1664; b) D. V. Yandulov, N. T. Tran, *J. Am. Chem. Soc.* **2007**, *129*, 1342–1358; c) T. Noel, T. J. Maimone, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2011**, *50*, 8900–8903; *Angew. Chem.* **2011**, *123*, 9062–9065.

[4] a) K. L. Hull, W. Q. Anani, M. S. Sanford, *J. Am. Chem. Soc.* **2006**, *128*, 7134–7135; b) X. Wang, T.-S. Mei, J.-Q. Yu, *J. Am. Chem. Soc.* **2009**, *131*, 7520–7521; c) K. S. L. Chan, M. Wasa, X. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2011**, *50*, 9081–9084; *Angew. Chem.* **2011**, *123*, 9247–9250; d) N. D. Ball, M. S. Sanford, *J. Am. Chem. Soc.* **2009**, *131*, 3796–3797; e) T. Furuya, H. M. Kaiser, T. Ritter, *Angew. Chem. Int. Ed.* **2008**, *47*, 5993–5996; *Angew. Chem.* **2008**, *120*, 6082–6085.

[5] a) B. M. Trost, D. L. Van Vranken, *Chem. Rev.* **1996**, *96*, 395–422; b) M. H. Katcher, A. G. Doyle, *J. Am. Chem. Soc.* **2010**, *132*, 17402–17404; c) M. H. Katcher, A. Sha, A. G. Doyle, *J. Am. Chem. Soc.* **2011**, *133*, 15902–15905; d) C. Hollingworth, A. Hazari, M. N. Hopkinson, M. Tredwell, E. Benedetto, M. Huiban, A. D. Gee, J. M. Brown, V. Gouverneur, *Angew. Chem. Int. Ed.* **2011**, *50*, 2613–2617; *Angew. Chem.* **2011**, *123*, 2661–2665.

[6] a) G. He, S. Qiu, H. Huang, G. Zhu, D. Zhang, R. Zhang, H. Zhu, *Org. Lett.* **2016**, *18*, 1856–1859; b) F. Nahra, S. R. Patrick, D. Bello, M. Brill, A. Obled, D. B. Cordes, A. M. Z. Slawin, D. O'Hagan, S. P. Nolan, *ChemCatChem* **2015**, *7*, 240–244.

[7] a) J. A. Akana, K. X. Bhattacharyya, P. Mueller, J. P. Sadighi, *J. Am. Chem. Soc.* **2007**, *129*, 7736–7737; b) B. C. Gorske, C. T. Mbofana, S. J. Miller, *Org. Lett.* **2009**, *11*, 4318–4321.

[8] O. E. Okoromoba, J. Han, G. B. Hammond, B. Xu, *J. Am. Chem. Soc.* **2014**, *136*, 14381–14384.

[9] a) T. Furuya, T. Ritter, *Org. Lett.* **2009**, *11*, 2860–2863; b) T. Furuya, A. E. Strom, T. Ritter, *J. Am. Chem. Soc.* **2009**, *131*, 1662–1663; c) P. Tang, T. Furuya, T. Ritter, *J. Am. Chem. Soc.* **2010**, *132*, 12150–12154.

[10] M. Schuler, F. Silva, C. Bobbio, A. Tessier, V. Gouverneur, *Angew. Chem. Int. Ed.* **2008**, *47*, 7927–7930; *Angew. Chem.* **2008**, *120*, 8045–8048.

[11] H. Peng, G. Liu, *Org. Lett.* **2011**, *13*, 772–775.

[12] a) S. Qiu, T. Xu, J. Zhou, Y. Guo, G. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 2856–2857; b) T. Xu, X. Mu, H. Peng, G. Liu, *Angew. Chem. Int. Ed.* **2011**, *50*, 8176–8179; *Angew. Chem.* **2011**, *123*, 8326–8329.

[13] a) V. V. Grushin, *Chem. Eur. J.* **2002**, *8*, 1006–1014; b) V. V. Grushin, W. J. Marshall, *Organometallics* **2007**, *26*, 4997–5002; c) V. V. Grushin, *Acc. Chem. Res.* **2010**, *43*, 160–171; d) N. P. Mankad, F. D. Toste, *Chem. Sci.* **2012**, *3*, 72–76.

[14] a) E. Emer, J. Twilton, M. Tredwell, S. Calderwood, T. L. Collier, B. Liégault, M. Taillefer, V. Gouverneur, *Org. Lett.* **2014**, *16*, 6004–6007; b) T. B. Patrick, J. J. Scheibel, G. L. Cantrell, *J. Org. Chem.* **1981**, *46*, 3917–3918.

[15] a) Y. Wang, M. E. Muratore, A. M. Echavarren, *Chem. Eur. J.* **2015**, *21*, 7332–7339; b) Y. Xi, Y. Su, Z. Yu, B. Dong, E. J. McClain, Y. Lan, X. Shi, *Angew. Chem. Int. Ed.* **2014**, *53*, 9817–9821; *Angew. Chem.* **2014**, *126*, 9975–9979; c) Y. Liu, Z. Yu, J. Z. Zhang, L. Liu, F. Xia, J. Zhang, *Chem. Sci.* **2016**, *7*, 1988–1995; d) L. Liu, J. Zhang, *Chem. Soc. Rev.* **2016**, *45*, 506–516; e) L. Nunes dos Santos Comprido, J. E. M. N. Klein, G. Knizia, J. Kästner, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2015**, *54*, 10336–10340; *Angew. Chem.* **2015**, *127*, 10477–10481; f) A. S. Hashmi, F. D. Toste, *Modern gold catalyzed synthesis*, Wiley-VCH, Weinheim, **2012**; g) F. D. Toste, V. Michelet, *Gold catalysis: an homogeneous approach*, Imperial College Press, London, **2014**.

[16] a) Y. Luo, K. Ji, Y. Li, L. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 17412–17415; b) W. He, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2011**, *133*, 8482–8485; c) L. Ye, W. He, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 8550–8551; d) L. Ye, L. Cui, G. Zhang, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 3258–3259; e) B. Lu, C. Li, L. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 14070–14072; f) W. He, L. Xie, Y. Xu, J. Xiang, L. Zhang, *Org. Biomol. Chem.* **2012**, *10*, 3168–3171; g) Y. Wang, K. Ji, S. Lan, L. Zhang, *Angew. Chem. Int. Ed.* **2012**, *51*, 1915–1918; *Angew. Chem.* **2012**, *124*, 1951–1954; h) H. Chen, L. Zhang, *Angew. Chem. Int. Ed.* **2015**, *54*, 11775–11779; *Angew. Chem.* **2015**, *127*, 11941–11945; i) Y.

Wang, Z. Zheng, L. Zhang, *J. Am. Chem. Soc.* **2015**, *137*, 5316 – 5319.
[17] a) R. K. Kawade, R.-S. Liu, *Org. Lett.* **2013**, *15*, 4094 – 4097; b) H.-H. Hung, Y.-C. Liao, R.-S. Liu, *J. Org. Chem.* **2013**, *78*, 7970 – 7976; c) S. Ghorpade, M.-D. Su, R.-S. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 4229 – 4234; *Angew. Chem.* **2013**, *125*, 4323 – 4328; d) E. P. A. Talbot, M. Richardson, J. M. McKenna, F. D. Toste, *Adv. Synth. Catal.* **2014**, *356*, 687 – 691; e) L. Wang, X. Xie, Y. Liu, *Angew. Chem. Int. Ed.* **2013**, *52*, 13302 – 13306; *Angew. Chem.* **2013**, *125*, 13544 – 13548; f) D. Qian, H. Hu, F. Liu, B. Tang, W. Ye, Y. Wang, J. Zhang, *Angew. Chem. Int. Ed.* **2014**, *53*, 13751 – 13755; *Angew. Chem.* **2014**, *126*, 13971 – 13975; g) J. Zhao, J. Liu, X. Xie, S. Li, Y. Liu, *Org. Lett.* **2015**, *17*, 5926 – 5929; h) M. Xu, T.-T. Ren, C.-Y. Li, *Org. Lett.* **2012**, *14*, 4902 – 4905; i) L. Xie, Z. Liang, D. Yan, W. He, J. Xiang, *Synlett* **2013**, *24*, 1809 – 1812.
[18] a) Y. Guo, B. Twamley, J. M. Shreeve, *Org. Biomol. Chem.* **2009**, *7*, 1716 – 1722; b) K.-Y. Kim, B. C. Kim, H. B. Lee, H. Shin, *J. Org. Chem.* **2008**, *73*, 8106 – 8108; c) G. K. S. Prakash, P. Beier, *Angew. Chem. Int. Ed.* **2006**, *45*, 2172 – 2174; *Angew. Chem.* **2006**, *118*, 2228 – 2230; d) E. C. Burger, B. R. Barron, J. A. Tunge, *Synlett* **2006**, 2824 – 2826; e) F. A. Davis, W. Han, C. K. Murphy, *J. Org. Chem.* **1995**, *60*, 4730 – 4737; f) W. R. Dolbier, Jr., S. K. Lee, O. I. V. Phanstiel, *Tetrahedron* **1991**, *47*, 2065 – 2072.
[19] a) T. D. Haro, C. Nevado, *Chem. Commun.* **2010**, *46*, 428 – 429; b) T. de Haro, C. Nevado, *Adv. Synth. Catal.* **2010**, *352*, 2767 – 2772.
[20] M. N. Hopkinson, G. T. Giuffredi, A. D. Gee, V. Gouverneur, *Synlett* **2010**, 2737 – 2742.
[21] J. P. Cain, P. L. Gassman, H. Wang, A. Laskin, *Phys. Chem. Chem. Phys.* **2010**, *12*, 5206 – 5218.
[22] Q. Yang, L.-L. Mao, B. Yang, S.-D. Yang, *Org. Lett.* **2014**, *16*, 3460 – 3463.
[23] W. Wang, G. B. Hammond, B. Xu, *J. Am. Chem. Soc.* **2012**, *134*, 5697 – 5705.
[24] Z. Lu, J. Han, G. B. Hammond, B. Xu, *Org. Lett.* **2015**, *17*, 4534 – 4537.
[25] P. T. Nyffeler, S. G. Duron, M. D. Burkart, S. P. Vincent, C.-H. Wong, *Angew. Chem. Int. Ed.* **2005**, *44*, 192 – 212; *Angew. Chem.* **2005**, *117*, 196 – 217.
[26] K. Tenza, J. S. Northen, D. O'Hagan, A. M. Z. Slawin, *J. Fluorine Chem.* **2004**, *125*, 1779 – 1790.
[27] Y. He, X. Zhang, N. Shen, X. Fan, *J. Fluorine Chem.* **2013**, *156*, 9 – 14.
[28] C. F. Bridge, D. O'Hagan, *J. Fluorine Chem.* **1997**, *82*, 21 – 24.
[29] T. H. K. Thvedt, E. Fuglseth, E. Sundby, B. H. Hoff, *Tetrahedron* **2010**, *66*, 6733 – 6743.
[30] Z. Xu, H. Chen, Z. Wang, A. Ying, L. Zhang, *J. Am. Chem. Soc.* **2016**, *138*, 5515 – 5518.

Received: April 22, 2016
Revised: June 12, 2016
Published online: July 20, 2016

