Angewandte
Zuschriften

Photoredox Catalysis

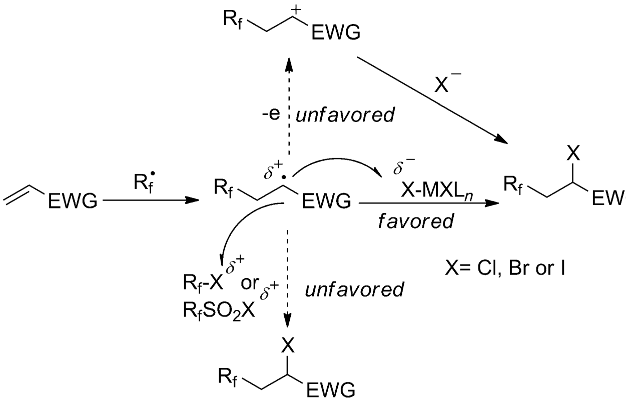
Deutsche Ausgabe: DOI: 10.1002/ange.201412199
Internationale Ausgabe: DOI: 10.1002/anie.201412199

Efficient Cu-catalyzed Atom Transfer Radical Addition Reactions of Fluoroalkylsulfonyl Chlorides with Electron-deficient Alkenes Induced by Visible Light**

*Xiao-Jun Tang and William R. Dolbier, Jr.**

Abstract: *Fluoroalkylsulfonyl chlorides, R_fSO_2Cl, in which $R_f = CF_3$, C_4F_9, CF_2H, CH_2F, and CH_2CF_3, are used as a source of fluorinated radicals to add fluoroalkyl groups to electron-deficient, unsaturated carbonyl compounds. Photochemical conditions, using Cu mediation, are used to produce the respective α-chloro-β-fluoroalkylcarbonyl products in excellent yields through an atom transfer radical addition (ATRA) process. Facile nucleophilic replacement of the α-chloro substituent is shown to lead to further diverse functionalization of the products.*

The unique physical and chemical properties of fluoroorganic compounds often bestow enhanced biological properties upon them compared to their nonfluorinated analogues. Therefore, fluorine-containing compounds continue to receive particular attention in the agrochemical, pharmaceutical, and material science industries.[1] Of the many ways to introduce fluorine-containing substituents into molecules, additions of fluorinated radicals to alkenes, alkynes, and arenes remain among the most direct and useful methods.[2] In particular, atom transfer radical addition (ATRA) reactions of R_fX ($X = I$, Br) to electron-rich alkenes is one such well-demonstrated methodology, which has been utilized frequently in recent decades. In these reactions the R_f radical is usually generated thermally by use of catalytic amounts of low-valent metals[3] or radical initiators such as $Na_2S_2O_4$,[4] azobisisobutyronitrile (AIBN),[5] benzoyl peroxide (BPO),[6] Et_3B/O_2,[7] or by use of reductive photocatalysts[8] to afford 1:1 adducts in high yields. Thus far, such methods have not proved useful for additions to electron-deficient alkenes, the use of which resulted in low conversion, selectivity, and yield, along with the formation of undesired byproducts and oligomers.[9] Recent attempts to improve yields of reactions of R_fI with electron-deficient alkenes by the use of UV light have been reported, but a large excess of R_fI and highly diluted reaction conditions were required.[10] In addition, elimination[10] and reduced products and oligomers[11] were commonly observed as significant byproducts. Such unsatisfactory results can be largely attributed to the electrophilic nature of the radical intermediate that is formed by addition of the fluorinated radical to the electron-deficient alkene (Scheme 1). Thus the rate of abstraction of the halogen atom from R_fX or R_fSO_2Cl by the electrophilic radical intermediate is diminished, chain propagation is inhibited, and the ATRA process is diverted to form alternative products. In addition, the impact of the adjacent electron-withdrawing group makes it energetically unfavorable for the radical to be oxidized to a corresponding carbocation that could be trapped by halide ions.



Scheme 1. ATRA reaction of the fluorinated radical with electron-deficient alkene.

Since the first $FeCl_2$-catalyzed ATRA reaction of CCl_4 with an electron-deficient alkene, acrylonitrile, was reported in 1956,[12] transition-metal (Ru[13] and Cu[14])-catalyzed ATRA/ATRP reactions of polychloroalkanes or activated alkyl halides with electron-rich or electron-deficient alkenes have become widely used in organic synthesis and polymerization. Thus far, due to the poor reducing ability of Ru or Cu species, fluoroalkyl halides have not proved very effective in such reactions, with useful reactions being mainly limited to easily reduced polyhalo, fluorinated alkanes, with temperatures as high as 140 °C being required in some cases.[15] In 1989, a Ru-catalyzed ATRA reaction using CF_3SO_2Cl was reported using ethyl acrylate as substrate to obtain a moderate yield of the desired 1:1 adduct.[16] However, because of the relatively poor reducing ability of $RuCl_2(PPh_3)_3$, this protocol required the use of a large excess of ethyl acrylate (5 equiv) along with high temperatures (120 °C) in benzene.

Over the last few years, photoredox catalysis has received much attention due to the excellent reducing ability of photocatalysts in the excited state.[17] Recently, we reported a general method of generating fluorinated radicals such as

---

[*] Dr. X.-J. Tang, Prof. Dr. W. R. Dolbier, Jr.
Department of Chemistry, University of Florida
PO Box 117200, Gainesville, Florida, 32611-7200 (USA)
E-mail: wrd@chem.ufl.edu

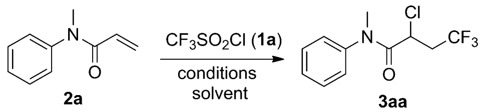
[**] Support of this research by a grant from Syngenta Crop Protection is gratefully acknowledged.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201412199.

CF_2H, CFH_2, and CF_3CH_2 from their corresponding fluoroalkylsulfonyl chlorides using photoredox catalysis under mild conditions.[18] On the basis of that work, we came to believe that photoinduced ATRA reactions of fluoroalkylsulfonyl chlorides with electron-deficient alkenes might be possible.

Using the reaction of CF_3SO_2Cl with *N*-methyl-*N*-phenylacrylamide (**2a**) as model reaction for exploratory experiments, we did not find reaction conditions that produce a significant yield of addition product when using either $Ru(phen)_3Cl_2$ or $Ru(bpy)_3Cl_2$ as catalysts (Table 1, entries 1–4), in spite of the fact that these catalysts had been effective in the ATRA reaction of CF_3SO_2Cl with electron-rich alkenes.[19] Also, not unexpectedly, simple thermally induced radical initiators, such as AIBN and dilauroyl peroxide (DLP) were also found to be ineffective in promoting the desired reaction (Table 1, entries 5 and 6), although we have recently found that similar reactions of fluoroalkylsulfonyl chlorides with electron-rich alkenes produced 1:1 adducts in high yields when using DLP as the radical initiator.[20]

Table 1: Exploratory experiments for reaction of CF_3SO_2Cl with *N*-methyl-*N*-phenylacrylamide.



Entry	Catalyst	Solvent	*T*	Yield[a]
1	1 mol% $Ru(phen)_3Cl_2$	MeCN	RT	trace
2	1 mol% $Ru(bpy)_3Cl_2$	MeCN	RT	trace
3	1 mol% $Ru(phen)_3Cl_2$	MeCN	RT	trace[b]
4	1 mol% $Ru(phen)_3Cl_2$	MeCN	RT	trace[c]
5	50 mol% AIBN	DCE	80°C	trace
6	50 mol% DLP	DCE	80°C	trace
7	1 mol% $Ir(ppy)_3$	MeCN	RT	44%
8	1 mol% $Ir(ppy)_3$	MeCN	RT	43%[b]
9	0.5 mol% $Cu(dap)_2Cl$	MeCN	RT	57%
10	0.5 mol% $Cu(dap)_2Cl$	DMF	RT	trace
11	0.5 mol% $Cu(dap)_2Cl$	DCM	RT	83%
12	0.5 mol% $Cu(dap)_2Cl$	DCM	RT	98% (94%[d])[b]
13	0.5 mol% $Cu(dap)_2Cl$	DCE	RT	98% (96%[d])[b]

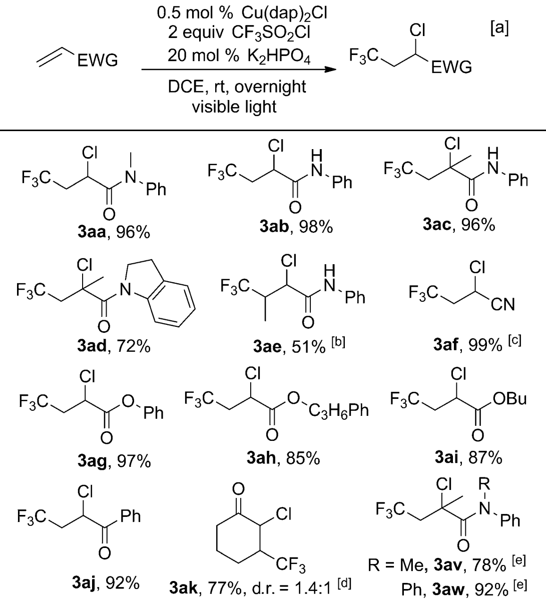
[a] All reactions were run with 0.3 mmol **2a** and 0.6 mmol CF_3SO_2Cl (**1a**) in 2 mL solvent for overnight under visible light except entries 5 and 6, and yields were determined by ^{19}F NMR spectroscopy using $PhCF_3$ as the internal standard. [b] 20 mol% K_2HPO_4 was used as the additive. [c] 100 mol% K_2HPO_4 was used as the additive. [d] The yields of isolated product **3aa** were based on **2a**. bpy = 2,2'-bipyridyl, dap = 2,9-bis(4-methoxyphenyl)-1,10-phenanthroline, DCE = 1,2-dichloroethane, DCM = dichloromethane, DMF = dimethylformamide, phen = 1,10-phenanthroline, ppy = 2-phenylpyridinato-C^2,*N*.

We were encouraged, however, to find that the use of $Ir(ppy)_3$ in place of the Ru catalysts led to a 43–44% yield of addition product (Table 1, entries 7 and 8). This result probably indicated that Ir^{IV} was a better mediative source of the Cl atom than was Ru^{III}.

Among all metal catalysts used in ATRA or atom transfer radical polymerization (ATRP) reactions, Cu species have been the most popular because of their effectiveness in mediating the transfer of the Cl atom.[21] Nevertheless, the poor redox potentials of commonly used Cu catalysts[22] made them unattractive as potential catalysts for reducing fluoroalkylsulfonyl chlorides. Recently, however, $Cu(dap)_2Cl$ was reported to be an efficient photocatalyst in the reaction of alkyl halides with electron-rich alkenes.[23] We thus speculated that $Cu(dap)_2Cl$, with its excellent reductive ability in the excited state ($E_{1/2}{}^{II/I*} = -1.42$ V vs. SCE in MeCN), combined with good Cl transfer properties, might be a good choice for initiating and propagating the ATRA reaction of fluoroalkylsulfonyl chlorides with electron-deficient alkenes. Indeed, the reaction of α,β-unsaturated amide **2a** with CF_3SO_2Cl in MeCN resulted in formation of the desired adduct **3aa** in 57% yield (Table 1, entry 9). Yields improved significantly when DCM was used as the solvent instead of MeCN (Table 1, entry 11). Lastly, the addition of 20 mol% K_2HPO_4, led to a virtually quantitative yield of **3aa** in either DCM or DCE (Table 1, entries 12 and 13).

Using these optimized conditions, reactions of CF_3SO_2Cl with various electron-deficient alkenes catalyzed by $Cu(dap)_2Cl$ under visible light were examined. As seen in Table 2, the preparation of α-chloro-β-trifluoromethyl amides, esters, and ketones were obtained from the respective unsaturated carbonyl substrates in moderate to excellent yields. The reactivity of α-substituted α,β-unsaturated amide **3ac** was comparable to that of the unsubstituted **3ab**. However, when the substrate was substituted at the β position, as in **3ae**, yields were reduced significantly. In particular, excellent yields of 1:1 adducts were obtained from

Table 2: Reactions of CF_3SO_2Cl with electron-deficient alkenes.

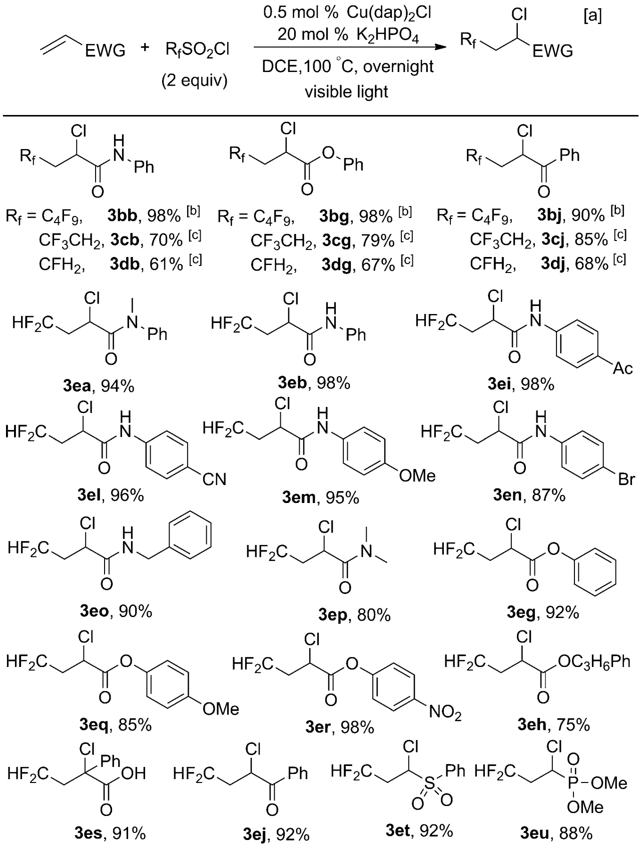


[a] Yields of isolated products were based on electron-deficient alkenes. [b] The reaction was run for 36 h; the yield as determined by ^{19}F NMR spectroscopy was 61% with a d.r. = 5:1. However, only one diastereoisomer was isolated successfully. [c] The reaction was run in DCM; the yield was determined by ^{19}F NMR spectroscopy. [d] The d.r. was 1:10 in the crude mixture, but was inverted and modified to 1.4:1 after purification by column chromatography on silica gel. [e] 1 equiv of K_2HPO_4 was used.

well-known, easily polymerizable acrylonitrile and *n*-butyl acrylate (**3af**, **3ai**). Likewise, comparison of the yields of esters **3ag**–**3ai** indicated that the reactivity of phenyl acrylate was greater than those of the alkyl acrylates. As for the *N*-arylmethacrylamide substrates **2v** or **2w**, which we have used previously in tandem radical cyclization studies,[18] ATRA adducts **3av** and **3aw** were still observed as the main products in 78% and 92% yields, respectively. It should be noted that CF_3Cl (^{19}F NMR: −28 ppm) was detected as a byproduct in all of these reactions. Its formation can be attributed to a competitive abstraction of the chlorine atom from CF_3SO_2Cl or the Cu^{II} species by the intermediate trifluoromethyl radical. In addition, because the reduction potential of CF_3SO_2Cl is much more positive than that of the resulting product, excess of the former can serve to prevent the latter from further reduction or polymerization.

This reaction was then extended to the use of other fluoroalkylsulfonyl chlorides, with the results being shown in Table 3. As expected, reactions of easily reduced $C_4F_9SO_2Cl$ with α,β-unsaturated amide, ester, and ketone gave the corresponding 1:1 adducts (**3bb**, **3bg**, and **3bj**) in excellent yields at room temperature. However, the reduction potentials of HCF_2SO_2Cl, H_2CFSO_2Cl, and $CF_3CH_2SO_2Cl$ are more negative than those of CF_3SO_2Cl and $C_4F_9SO_2Cl$, and therefore their reactions required higher temperatures. H_2CFSO_2Cl and $CF_3CH_2SO_2Cl$ underwent reaction with α,β-unsaturated amides, esters, and ketones to produce 1:1 adducts in good yields when the reaction temperature was increased to 110°C (**3cb**–**3cj** and **3db**–**3dj**). At higher temperatures, the rate of abstraction of the chlorine atom from the fluoroalkylsulfonyl chlorides or Cu^{II} species by the fluorinated radicals increased, which decreased the overall yields of the 1:1 adducts. Due to the importance of the CF_2H group, our examination of the scope of substrates used in reactions with HCF_2SO_2Cl was more extensive. In most cases, excellent yields of 1:1 adducts bearing CF_2H were obtained in reactions with electron-deficient alkenes at 100°C. Substituents such as −CN, −Ac, −Br, −OMe, and $-NO_2$ on phenyl were well-tolerated in these reactions. Notably, the reaction of α,β-unsaturated carboxylic acid (**2s**) with HCF_2SO_2Cl led to the desired adduct in 92% yield. Furthermore, use of α,β-unsaturated sulfone and phosphonate substrates, **2t** and **2u**, afforded the corresponding products in 92% and 88% yield, respectively.

Table 3: Reactions of R_fSO_2Cl with electron-deficient alkenes.



R_f = C_4F_9, **3bb**, 98% [b]; CF_3CH_2, **3cb**, 70% [c]; CFH_2, **3db**, 61% [c]

R_f = C_4F_9, **3bg**, 98% [b]; CF_3CH_2, **3cg**, 79% [c]; CFH_2, **3dg**, 67% [c]

R_f = C_4F_9, **3bj**, 90% [b]; CF_3CH_2, **3cj**, 85% [c]; CFH_2, **3dj**, 68% [c]

3ea, 94%; **3eb**, 98%; **3ei**, 98%

3el, 96%; **3em**, 95%; **3en**, 87%

3eo, 90%; **3ep**, 80%; **3eg**, 92%

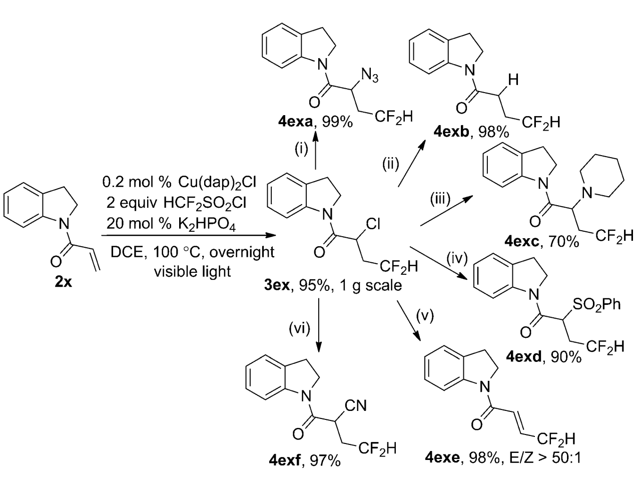
3eq, 85%; **3er**, 98%; **3eh**, 75%

3es, 91%; **3ej**, 92%; **3et**, 92%; **3eu**, 88%

[a] Yields of isolated products were based on electron-deficient alkenes. [b] Reactions were run at room temperature. [c] Reactions were run at 110°C.

Finally, expanded synthetic applications were explored using α,β-unsaturated amide **2x**. The reaction of **2x** with HCF_2SO_2Cl gave **3ex** in 95% yield on a 1 gram scale in the presence of 0.2 mol% $Cu(dap)_2Cl$. The C−Cl bond of **3ex** is much more reactive than a simple secondary C−Cl bond, and we have found it to be useful for performing further synthetic elaborations. As seen in Scheme 2, **3ex** undergoes many useful transformations such as reduction, elimination, and substitution by N_3, CN, amine, and sulfinate in high yields (**4exa**–**4exf**).

In conclusion, general and highly effective, Cu-catalyzed ATRA reactions of fluoroalkylsulfonyl chlorides with electron-deficient alkenes have been achieved. This reaction can be applied to a variety of fluoroalkylsulfonyl chlorides, including CF_3SO_2Cl, $C_4F_9SO_2Cl$, CF_2HSO_2Cl, CH_2FSO_2Cl, and $CF_3CH_2SO_2Cl$, in reaction with various electron-deficient alkenes such as α,β-unsaturated ketones, amides, esters, carboxylic acids, sulfone, and phosphonate. Because the α-chloro-β-fluoroalkylcarbonyl products all have an activated



Scheme 2. Further transformations of **3ex**. i) NaN_3, DMSO, 75°C, 3 h; ii) Zn, HOAc, RT, 3 h; iii) piperidine (neat), 45°C, 6 h; iv) $PhSO_2Na$, DMSO, 80°C, 45 min; v) DBU, toluene, reflux, 12 h; vi) NaCN, DMSO, 80°C, 3 h. DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, DMSO = dimethylsulfoxide.

α C–Cl bond, they can be further transformed into fluorinated amino acids, alkenes, and other useful derivatives.

Keywords: atom transfer radical addition reactions · copper · fluorine · photoredox catalysis · radicals

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 4246–4249
Angew. Chem. **2015**, *127*, 4320–4323

[1] For some reviews, see: a) D. O'Hagan, *Chem. Soc. Rev.* **2008**, *37*, 308–319; b) P. Kirsch, *Modern Fluoroorganic Chemistry*, Wiley-VCH, Weinheim, **2004**; c) I. Ojima, *Fluorine in Medicinal Chemistry and Chemical Biology*, Wiley-Blackwell, Chichester, **2009**; d) K. Uneyama, *Organofluorine Chemistry*, Blackwell, Oxford, **2006**; e) G. K. S. Prakash, S. Chacko, *Curr. Opin. Drug Discovery Dev.* **2008**, *11*, 793–802.

[2] For a review on reactivity of fluorinated radicals, see: a) W. R. Dolbier, Jr., *Chem. Rev.* **1996**, *96*, 1557–1584. In particular, for recent reviews on reactions of the trifluoromethyl radical, see: b) J. Xu, X. Liu, Y. Fu, *Tetrahedron Lett.* **2014**, *55*, 585–594; c) E. Merino, C. Nevado, *Chem. Soc. Rev.* **2014**, *43*, 6598–6608; d) T. Koike, M. Akita, *J. Fluorine Chem.* **2014**, *167*, 30–36; e) H. Egami, M. Sodeoka, *Angew. Chem. Int. Ed.* **2014**, *53*, 8294–8308; *Angew. Chem.* **2014**, *126*, 8434–8449.

[3] For selected reports, see: a) Z. Yang, D. J. Burton, *Tetrahedron Lett.* **1991**, *32*, 1019–1022; b) M. Kuroboshi, T. Ishihara, *J. Fluorine Chem.* **1988**, *39*, 299–303; c) C. R. Davis, D. J. Burton, Z. Yang, *J. Fluorine Chem.* **1995**, *70*, 135–140; d) Q. Chen, Z. Yang, *J. Chem. Soc. Chem. Commun.* **1986**, 498–499; e) Q. Chen, Y. He, Z. Yang, *J. Fluorine Chem.* **1986**, *34*, 255–258; f) Z. Yang, D. J. Burton, *J. Org. Chem.* **1992**, *57*, 5144–5149; g) T. Takagi, T. Kanamori, *J. Fluorine Chem.* **2011**, *132*, 427–429.

[4] For a review, see: C. Zhang, Q. Chen, Y. Guo, J. Xiao, Y. Gu, *Chem. Soc. Rev.* **2012**, *41*, 4536–4559.

[5] For pioneering work, see: a) N. O. Brace, *J. Org. Chem.* **1962**, *27*, 4491–4498; b) N. O. Brace, *J. Org. Chem.* **1967**, *32*, 430–434.

[6] For pioneering work, see: a) J. D. Park, F. E. Rogers, J. R. Lacher, *J. Org. Chem.* **1961**, *26*, 2089–2095; b) N. O. Brace, *J. Fluorine Chem.* **1982**, *20*, 313–327.

[7] a) Y. Takeyama, Y. Ichinose, K. Oshima, K. Utimoto, *Tetrahedron Lett.* **1989**, *30*, 3159–3162; b) W. Qiu, D. J. Burton, *J. Fluorine Chem.* **1993**, *62*, 273–281.

[8] a) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2011**, *133*, 4160–4163; b) C. J. Wallentin, J. D. Nguyen, P. Finkbeiner, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2012**, *134*, 8875–8884.

[9] a) R. N. Haszeldine, B. R. Steele, *J. Chem. Soc.* **1953**, 1199–1206; b) S. Elsheimer, W. R. Dolbier, Jr., M. Murla, *J. Org. Chem.* **1984**, *49*, 205–207.

[10] a) T. Yajima, H. Nagano, *Org. Lett.* **2007**, *9*, 2513–2515; b) T. Yajima, I. Jahan, T. Tonoi, M. Shinmen, A. Nishikawa, K. Yamaguchi, I. Sekine, H. Nagano, *Tetrahedron* **2012**, *68*, 6856–6861.

[11] a) Z. Qiu, D. J. Burton, *Tetrahedron Lett.* **1994**, *35*, 1813–1816; b) Z. Qiu, D. J. Burton, *J. Org. Chem.* **1996**, *60*, 6798–6805.

[12] F. Minisci, U. Pallini, E. Volterra, A. Quilico, *Chim. Hd.* **1956**, *38*, 371–382.

[13] For selected reports on Ru-catalyzed ATRA reactions, see: a) H. Matsumoto, T. Nikaido, *J. Org. Chem.* **1976**, *41*, 396–398; b) J. A. Tallarico, L. Malnick, M. L. Snapper, *J. Org. Chem.* **1999**, *64*, 344–345; c) F. Simal, L. Wlodarczak, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **2000**, *41*, 6071–6074; d) B. A. Seigal, C. Fajardo, M. L. Snapper, *J. Am. Chem. Soc.* **2005**, *127*, 16329–16332; e) L. Quebatte, K. Thommes, K. Severin, *J. Am. Chem. Soc.* **2006**, *128*, 7440–7441; f) K. Thommes, B. Icli, R. Scopelliti, K. Severin, *Chem. Eur. J.* **2007**, *13*, 6899–6907.

[14] For selected reviews on Cu-catalyzed ATRA/ATRP reactions, see: a) T. Pintauer, K. Matyjaszewski, *Chem. Soc. Rev.* **2008**, *37*, 1087–1097; b) N. V. Tsarevsky, K. Matyjaszewski, *Chem. Rev.* **2007**, *107*, 2270–2299; c) M. Ouchi, T. Terashima, M. Sawamoto, *Chem. Rev.* **2009**, *109*, 4963–5050; d) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921–2990.

[15] a) X. Tang, Q. Chen, *Org. Lett.* **2012**, *14*, 6214–6217; b) M. V. D. Puy, *J. Fluorine Chem.* **1993**, *61*, 133–140; c) B. Boutevin, Y. Hervaud, Y. Pietrasanta, *Phosphorus Sulfur Relat. Elem.* **1984**, *20*, 189–196; d) D. J. Burton, L. J. Kehoe, *J. Org. Chem.* **1970**, *35*, 1339–1342.

[16] a) N. Kamigata, T. Fukushima, Y. Terakawa, M. Yoshida, H. Sawada, *J. Chem. Soc. Perkin Trans. 1* **1991**, 627–633; b) N. Kamigata, T. Fukushima, M. Yoshida, *J. Chem. Soc. Chem. Commun.* **1989**, 1559–1560.

[17] For reviews, see: a) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; b) J. Xuan, W. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828–6838; *Angew. Chem.* **2012**, *124*, 6934–6944.

[18] X. Tang, C. S. Thomoson, W. R. Dolbier, Jr., *Org. Lett.* **2014**, *16*, 4594–4597.

[19] S. H. Oh, Y. R. Malpani, N. Ha, Y. Jung, S. Han, *Org. Lett.* **2014**, *16*, 1310–1313.

[20] C. S. Thomoson, X. Tang, W. R. Dolbier, Jr., *J. Org. Chem.* **2015**, *80*, 1264–1268.

[21] For a detailed mechanism study on Cu-catalyzed ATRA/ATRP reactions, see: A. A. Isse, A. Gennaro, C. Lin, J. L. Hodgson, M. L. Coote, T. Guliashvili, *J. Am. Chem. Soc.* **2011**, *133*, 6254–6264.

[22] To the best of our knowledge, with other ligands bound to Cu, the most negative $E_{1/2}^{\mathrm{II/I}}$ is about -0.7 V vs. SCE in MeCN; for some reports, see: a) C. Zhang, S. Kaderli, M. Costas, E. Kim, Y. Neuhold, K. D. Karlin, A. D. Zuberbuehler, *Inorg. Chem.* **2003**, *42*, 1807–1824; b) C. Zhang, H. Liang, E. Kim, J. Shearer, M. E. Helton, S. Kaderli, C. D. Incarvito, A. D. Zuberbuehler, A. L. Rheingold, K. D. Karlin, *J. Am. Chem. Soc.* **2003**, *125*, 634–635; c) L. Q. Hatcher, M. A. Vance, A. A. N. Sarjeant, E. I. Solomon, K. D. Karlin, *Inorg. Chem.* **2006**, *45*, 3004–3013.

[23] a) M. Pirtsch, S. Paria, T. Matsuno, H. Isobe, O. Reiser, *Chem. Eur. J.* **2012**, *18*, 7336–7340; b) M. Pirtsch, S. Paria, T. Matsuno, H. Isobe, O. Reiser, *Synthesis* **2013**, 2689–2698.

Received: December 19, 2014