Organic LETTERS

Letter

pubs.acs.org/OrgLett

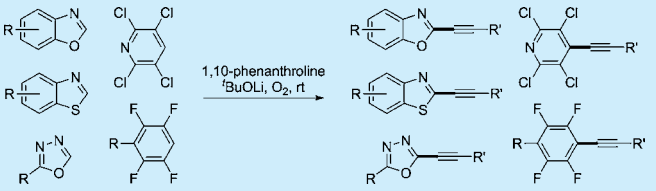
Room-Temperature Direct Alkynylation of Arenes with Copper Acetylides

Cédric Theunissen and Gwilherm Evano*

Laboratoire de Chimie Organique, Service de Chimie et PhysicoChimie Organiques, Université Libre de Bruxelles (ULB), Avenue F. D. Roosevelt 50, CP160/06, 1050 Brussels, Belgium

Supporting Information

ABSTRACT: C−H bond in azoles and polyhalogenated arenes can be smoothly activated by copper acetylides to give the corresponding alkynylated (hetero)arenes by simple reaction at room temperature in the presence of phenanthroline and lithium *tert*-butoxide under an oxygen atmosphere. These stable, unreactive, and readily available polymers act as especially efficient and practical reagents for the introduction of an alkyne group to a wide number of arenes under remarkably mild conditions.



In addition to being commonly found in naturally occurring/bioactive molecules as well as organic materials and polymers, alkynyl(hetero)arenes are also versatile building blocks and intermediates in organic synthesis, notably due to numerous possible synthetic transformations of the alkyne subunit.[1] The common method for the installation of an alkyne into arenes is the Sonogashira−Linstrumelle cross-coupling[2] which, despite its efficiency, requires the prefunctionalization of the aromatic ring. Recently, the direct alkynylation of C−H bonds in arenes has emerged as an especially straightforward and appealing alternative and various reagents, in combination with different metals, have been used for such transformations.[3] They include terminal alkynes,[4] alkynyl halides,[5] *gem*-dihaloalkenes,[6] arylsulfonylacetylenes,[7] propiolic acids,[8] or benzodioxolone-based hypervalent alkynyl iodonium salts[9] and can be used for the direct alkynylation of different classes of arenes with varying efficiency.

In the case of electron-deficient arenes such as azoles and polyfluoroarenes (whose prefunctionalization is far from trivial) several copper-,[4c−e,5f,g,6a,b] palladium-,[4g−i,5i,6c] nickel-,[4d,5c] and iron-[4f] based systems have been reported for the direct alkynylation of acidic C−H bonds in such systems. Due to the importance of the resulting alkynylated arenes in medicinal and agrochemical chemistry, as exemplified with representative examples **1**−**4** shown in Figure 1,[10−13] this C−H alkynylation strategy is quite appealing. However, despite their efficiency, all systems reported to date still suffer from major limitations, the main ones being the requirement for high temperatures, lack of practicability, and poor substrate scope. Alternative methods/reagents that would allow for an efficient and practical direct alkynylation of electron-deficient arenes under mild conditions are therefore highly desirable. In this perspective, we report that copper acetylides, readily available reagents that are known to be remarkably stable and especially unreactive,[14] can be efficiently used for the direct alkynylation of azoles and polyfluoroarenes at room temperature.

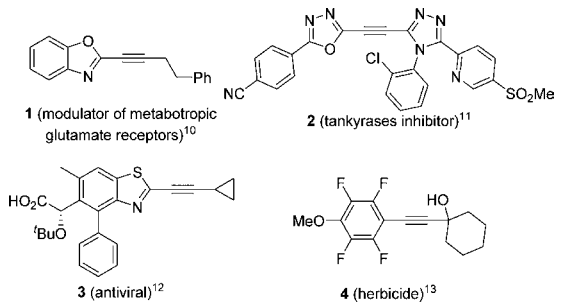


Figure 1. Representative bioactive alkynylated azoles and polyfluoroarenes.

We have indeed recently shown that copper acetylides can be easily activated in the presence of molecular oxygen and simple organic ligands and transfer their alkyne subunit to a wide range of heteronucleophiles[15] following an oxidative umpolung strategy.[16,17] On the basis of the success met with this strategy, we envisioned that they might also be suitable reagents for the direct room-temperature alkynylation of (hetero)arenes possessing relatively acidic C−H bonds such as azoles and polyfluoroarenes, a strategy that was supported by results from the Knochel group who demonstrated the possibility of an oxidative copper-mediated cross-coupling between alkynyl lithium and aryl magnesium reagents.[17d]

To test this hypothesis, we initiated our studies by examining the oxidative cross-coupling between (*p*-tolylethynyl)copper **6a** and benzoxazole **5a**, the latter being used in excess to minimize the homocoupling of the former. For practical reasons, the temperature was fixed at room temperature, and molecular oxygen was chosen as the oxidant. Lithium *tert*-butoxide was used to assist the cleavage of the acidic C−H bond in **5a**, and a brief solvent screen using TMEDA as the ligand revealed that

Received: July 11, 2014
Published: August 12, 2014

dx.doi.org/10.1021/ol502030y | *Org. Lett.* 2014, 16, 4488−4491

the reaction was best performed in acetonitrile. The efficiency of various ligands susceptible to promote the oxidative cross-coupling was evaluated, and while electron-rich nitrogen ligands were found to be somehow more efficient than the other ones studied, the alkynylation turned out to be quite challenging (Figure 2). Assuming that multiple chelation of the

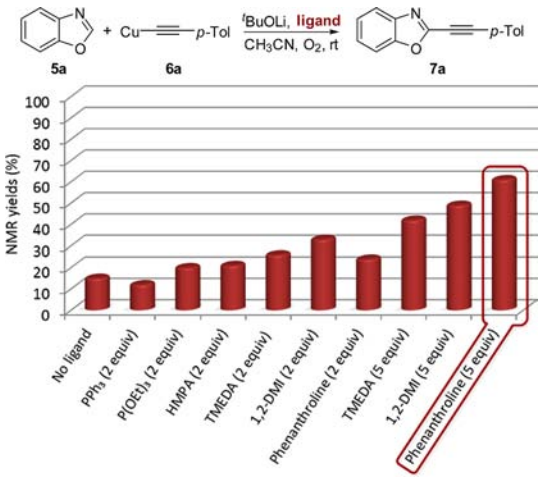


Figure 2. Compared efficiency of ligands for the alkynylation of benzoxazole.

deprotonated benzoxazole to the copper center might account for the low yields obtained, we decided to check whether increasing the amount of the ligand would have a beneficial effect on the alkynylation. To our delight, the alkynylation could indeed be improved when using an excess of TMEDA, 1,2-dimethylimidazole, or 1,10-phenanthroline, the latter being superior in terms of efficiency. By using these optimized conditions, the alkynylation could then be readily achieved by simply adding the corresponding copper acetylide to a mixture of the starting benzoxazole, lithium *tert*-butoxide, and 1,10-phenanthroline in acetonitrile at room temperature. Upon activation with molecular oxygen at room-temperature, the alkynylation occurs, and the completion of the reaction can be easily detected due to the self-indicating nature of the reaction in which the starting bright-yellow polymeric copper acetylide slowly dissolves to yield a brownish solution.

With these conditions in hand, we moved to the evaluation of the scope and limitations of this oxidative alkynylation using a set of representative benzoxazoles/benzothiazole **5** and copper acetylides **6** (Figure 3). The reaction proceeded smoothly in most cases, and the yields of the resulting alkynylated azoles **7** were found to be comparable to the ones

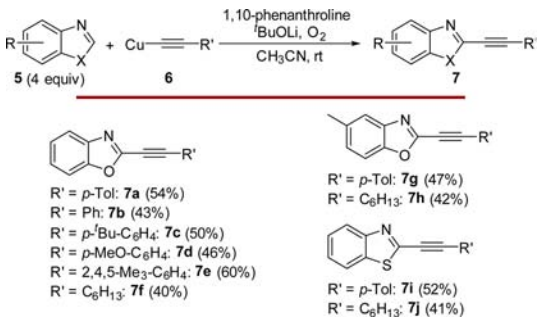


Figure 3. Direct alkynylation of benzoxazoles and benzothiazole.

obtained using a halogenation/Sonogashira sequence[18] or with other direct alkynylation procedures.[4d,f−h,5c,g,j,6a,c] The reaction enabled the synthesis of aryl-substituted alkynyl-benzoxazoles (**7a−e,g**) and benzothiazoles (**7i**) as well as their alkyl-substituted congeners (**7f,h,j**), and benzoxazoles and benzothiazole were found to be equally efficient. Interestingly, while the homodimerization of the starting copper acetylides could not be completely suppressed, the copper-mediated dimerization of the starting azoles, which had been previously documented,[19] was found to be quite slow in our case.

Given the operational simplicity of this oxidative alkynylation, we then decided to evaluate the use of other azoles in this procedure. Due to the importance of 1,3,4-oxadiazoles in medicinal chemistry[20] and in material sciences,[21] we logically decided to study their alkynylation using our standard procedure. Results from these studies provide evidence that the reaction proceeds quite smoothly in most cases, the alkynylated 1,3,4-oxadiazoles **9** being easily isolated in moderate to good yields (Figure 4). In the case of aryl-

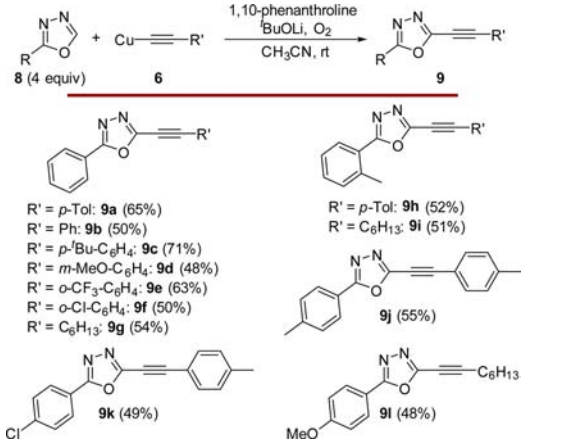


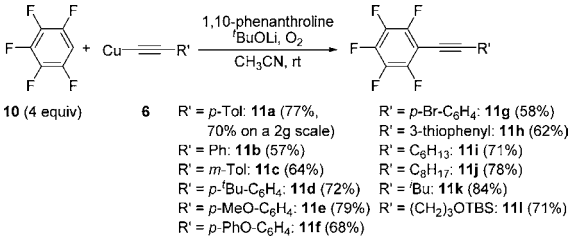
Figure 4. Direct alkynylation of 1,3,4-oxadiazoles.

substituted alkynylcopper reagents and oxadiazoles, the nature of the substituents on both the oxadiazole **8** and the copper acetylide **6** was found to have little influence on the outcome of the reaction which proceeded with equal efficiency in the presence of electron-donating and -withdrawing groups in the *ortho*, *meta*, or *para* positions. Alkyl-substituted copper acetylides could also be used for the oxidative alkynylation at room temperature, yielding the corresponding alkyl-substituted 2-alkynyl-1,3,4-oxadiazoles (**9g,i,l**) with synthetically useful yields under practical conditions.

We next moved to study other arenes possessing an activated acidic C−H bond: polyfluoroarenes. The pK_a value of its C(sp2)−H bond being in the same range as those of azoles,[22] pentafluorobenzene **10** was therefore reacted with various copper acetylides **6** and was transformed to the corresponding alkynyl-pentafluorobenzene derivatives **11**, building blocks of great interest for electronic and optoelectronic applications,[23] with high efficiency (Scheme 1). Even an aromatic bromide was well tolerated on the starting copper acetylide, therefore providing an excellent starting point for further derivatization starting from **11g**. Importantly, the reaction could be performed with alkyl-substituted alkynylcopper reagents, products **11i−l** resulting from the oxidative cross-coupling being obtained in good yields with our procedure while they could not be obtained using previously reported ones.[3c,d]

dx.doi.org/10.1021/ol502030y | *Org. Lett.* 2014, 16, 4488−4491

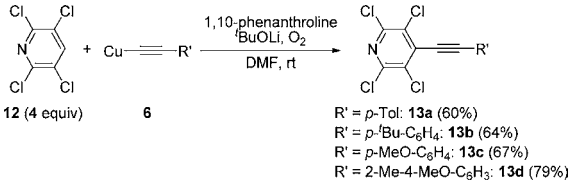
Scheme 1. Direct Alkynylation of Pentafluorobenzene



Finally, it should be mentioned that the reaction can be conveniently performed on a 2 g scale (for the synthesis of **11a**) without significant decrease of yield.

The reaction could also be extended to the direct alkynylation of tetrachloropyridine **12**, in which the presence of activated chlorine atoms, susceptible to undergoing competitive nucleophilic aromatic substitution even with weak nucleophiles, clearly rendered the direct alkynylation more challenging. The oxidative alkynylation proceeded smoothly upon reaction with various copper acetylides **6** under our standard conditions without competitive nucleophilic aromatic substitution by the copper acetylide or lithium *tert*-butoxide (Scheme 2). The corresponding alkynylated tetra-

Scheme 2. Direct Alkynylation of and Tetrachloropyridine



chloropyridines **13**, in which the activated chlorine atoms at C2 and C6 provide excellent starting points for further derivatization by nucleophilic aromatic substitution or metal-catalyzed cross-coupling reactions, could be isolated in good yields.

To further test the synthetic potential of our oxidative alkynylation, we next decided to investigate the possibility of using our procedure for the alkynylation starting from more complex arenes or copper acetylides. With this goal in mind, the direct alkynylation of a cholic acid-derived 1,3,4-oxadiazole was first evaluated and smoothly provided the corresponding alkynylated derivative **9m** in 46% yield, even by using 1.5 equiv of the oxadiazole instead of the 4 equiv used for the scope and limitation studies (Figure 5). Placing the molecular complexity on the starting copper acetylide turned out to be even more

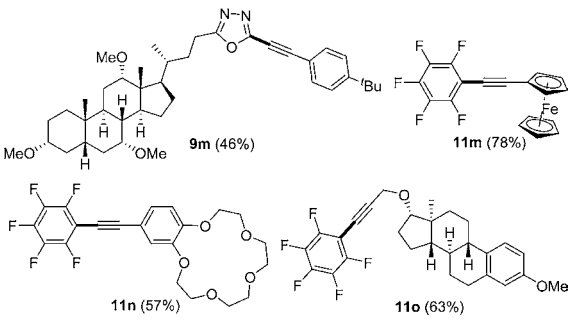
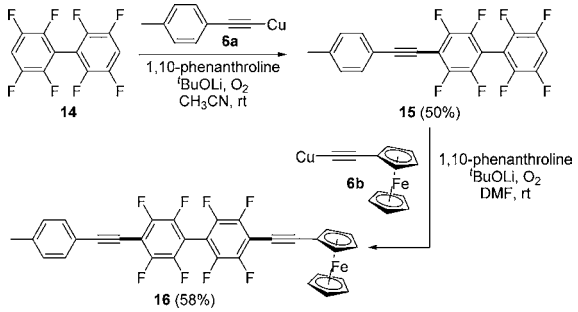


Figure 5. Direct alkynylation with complex substrates.

efficient, as demonstrated by the reaction of ferrocene-, benzocrown ether-, and estradiol-derived copper acetylides with pentafluorobenzene which nicely provided the corresponding alkynylated products **11m–o**, further showing the beneficial output of using copper acetylides for the direct alkynylation of arenes under mild conditions.

We finally moved one step further and briefly investigated the possibility of a double consecutive alkynylation. Octafluorobiphenyl **14** was thus first monoalkynylated with **6a**, providing the corresponding alkynyl-octafluorobiphenyl **15** (Scheme 3). The remaining acidic C–H bond in this

Scheme 3. Consecutive Double Oxidative Alkynylations



compound could then be used for the introduction of a different alkyne, and a second oxidative alkynylation with **6b** could indeed be performed, yielding the desired diyne **16** resulting from two double consecutive alkynylations.

In conclusion, we have developed an efficient and general procedure for the direct oxidative alkynylation of activated C–H bonds in arenes. Upon reaction with readily prepared and otherwise unreactive copper acetylides in the presence of lithium *tert*-butoxide and phenanthroline, a wide variety of arenes possessing an acidic C–H bond such as azoles and polyhalogenated arenes could be smoothly alkynylated at room temperature. Molecular oxygen is sufficient to trigger the alkynylation which provides an efficient entry to numbers of alkynyl-(hetero)arenes, versatile building blocks and intermediates in organic synthesis, that are also at the core structure of various naturally occurring and/or bioactive molecules as well as organic materials and polymers. Major advantages of this direct oxidative alkynylation, which does not require prefunctionalization of the starting arene, are the mild and practical conditions that do not require thermal activation, its scope, its modularity, and its use for the alkynylation with complex substrates and double consecutive alkynylations. This reaction can in addition be performed without precautions or inert atmosphere, does not require the use of expensive chemicals, and typically affords the alkynylated (hetero)arenes with improved yields, reaction conditions, or substrate scope in most cases compared to previously reported catalytic direct alkynylations. We envision great acceptance and applicability for this oxidative cross-coupling reaction, and further studies are underway in our laboratory to extend its scope.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization, copies of ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/ol502030y | Org. Lett. 2014, 16, 4488–4491

AUTHOR INFORMATION

Corresponding Author

*gevano@ulb.ac.be

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Our work was supported by the Université Libre de Bruxelles and the FNRS (Incentive Grant for Scientific Research no. F.4530.13). C.T. acknowledges the Fonds pour la formation à la Recherche dans l'Industrie et dans l'Agriculture (F.R.I.A.) for a graduate fellowship.

REFERENCES

(1) *Acetylene Chemistry: Chemistry, Biology and Material Science*; Diedrich, F., Stang, P. J., Tywinski, R. R., Eds.; Wiley-VCH: Weinheim, 2005.

(2) Chinchilla, R.; Nájera, C. *Chem. Soc. Rev.* **2011**, *40*, 5084.

(3) For selected reviews addressing the direct alkynylation of C-H bonds in arenes, see: (a) Dudnik, A. S.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 2096. (b) Mesaoudi, S.; Brion, J.-D.; Alami, M. *Eur. J. Org. Chem.* **2010**, 6495. (c) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 10236. (d) Rouquet, G.; Chatani, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 11726.

(4) (a) de Haro, T.; Nevado, C. *J. Am. Chem. Soc.* **2010**, *132*, 1512. (b) Yang, L.; Zhao, L.; Li, C.-J. *Chem. Commun.* **2010**, *46*, 4184. (c) Wei, Y.; Zhao, H.; Kan, J.; Su, W.; Hong, M. *J. Am. Chem. Soc.* **2010**, *132*, 2522. (d) Matsuyama, N.; Kitahara, M.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2010**, *12*, 2358. (e) Kitahara, M.; Hirano, K.; Tsurugi, H.; Satoh, T.; Miura, M. *Chem.—Eur. J.* **2010**, *16*, 1772. (f) Patil, S. S.; Jadhav, R. P.; Patil, S. V.; Bobade, V. D. *Tetrahedron Lett.* **2011**, *52*, 5617. (g) Kim, S. H.; Yoon, J.; Chang, S. *Org. Lett.* **2011**, *13*, 1474. (h) Shibahara, F.; Dohke, Y.; Murai, T. *J. Org. Chem.* **2012**, *77*, 5381. (i) Kim, S. H.; Park, S. H.; Chang, S. *Tetrahedron* **2012**, *68*, 5162. (j) Jie, X.; Shang, Y.; Hu, P.; Su, W. *Angew. Chem., Int. Ed.* **2013**, *52*, 3630.

(5) (a) Kobayashi, K.; Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2002**, *124*, 8528. (b) Seregin, I. V.; Ryabova, V.; Gevorgyan, V. *J. Am. Chem. Soc.* **2007**, *129*, 7742. (c) Matsuyama, N.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 4156. (d) Tobisu, M.; Ano, Y.; Chatani, N. *Org. Lett.* **2009**, *11*, 3250. (e) Gu, Y.; Wang, X. *Tetrahedron Lett.* **2009**, *50*, 763. (f) Besselièvre, F.; Piguel, S. *Angew. Chem., Int. Ed.* **2009**, *48*, 9553. (g) Kawano, T.; Matsuyama, N.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2010**, *75*, 1764. (h) Dudnik, A. S.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2010**, *49*, 2096. (i) Kim, S. H.; Chang, S. *Org. Lett.* **2010**, *12*, 1868. (j) Ano, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2012**, *14*, 354. (k) Zhao, Y.; He, G.; Nack, W. A.; Chen, G. *Org. Lett.* **2012**, *14*, 2948. (l) Ano, Y.; Tobisu, M.; Chatani, N. *Synlett* **2012**, *23*, 2763.

(6) (a) Berciano, B. P.; Lebrequier, S.; Besselièvre, F.; Piguel, S. *Org. Lett.* **2010**, *12*, 4038. (b) Reddy, G. C.; Balasubramanayam, P.; Salvanna, N.; Das, B. *Eur. J. Org. Chem.* **2012**, 471. (c) Ackermann, L.; Komhaass, C.; Zhu, Y. *Org. Lett.* **2012**, *14*, 1824.

(7) (a) García Ruano, J. L.; Alemán, J.; Marzo, L.; Alvarado, C.; Tortosa, M.; Díaz-Tendero, S.; Fraile, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 2712. (b) García Ruano, J. L.; Alemán, J.; Marzo, L.; Alvarado, C.; Tortosa, M.; Díaz-Tendero, S.; Fraile, A. *Chem.—Eur. J.* **2012**, *18*, 8414.

(8) Kim, J.; Kang, D.; Yoo, E. J.; Lee, P. H. *Eur. J. Org. Chem.* **2013**, 7902.

(9) (a) Brand, J. P.; Charpentier, J.; Waser, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 9346. (b) Brand, J. P.; Waser, J. *Angew. Chem., Int. Ed.* **2010**, *49*, 7304. (c) Brand, J. P.; Chevalley, C.; Scopelliti, R.; Waser, J. *Chem.—Eur. J.* **2012**, *18*, 5655. (d) Brand, J. P.; Waser, J. *Org. Lett.* **2012**, *14*, 744. (e) Liu, X.; Wang, Z.; Cheng, X.; Li, C. *J. Am. Chem. Soc.* **2012**, *134*, 14330. (f) Brand, J. P.; Waser, J. *Synthesis* **2012**, *44*, 1155. (g) Li, Y.; Brand, J. P.; Waser, J. *Angew. Chem., Int. Ed.* **2013**, *52*, 6743.

(10) Bessis, A.-S.; Bolea, C.; Bonnet, B.; Epping-Jordan, M.; Poirier, N.; Poli, S.-M.; Rocher, J.-P.; Thollon, Y. world patent WO2005123703(A2), December 29, 2005.

(11) Voronkov, A.; Holsworth, D. D.; Waaler, J.; Wilson, S. R.; Ekblad, B.; Perdreau-Dahl, H.; Dinh, H.; Drewes, G.; Hopf, C.; Morth, J. P.; Kraus, S. *J. Med. Chem.* **2013**, *56*, 3012.

(12) Mitchell, M. L.; Roethle, P. A.; Xu, L.; Yang, H.; McFadden, R.; Babaoglu, K. world patent WO/2012/145728(A1), October 26, 2012.

(13) Parlow, J. J.; Clark, R. D. *J. Agric. Food Chem.* **1994**, *42*, 2600.

(14) Normant, J. F. *Synthesis* **1981**, 63.

(15) (a) Jouvin, K.; Heimburger, J.; Evano, G. *Chem. Sci.* **2012**, *3*, 756. (b) Laouiti, A.; Jouvin, K.; Rammah, M. M.; Rammah, M. B.; Evano, G. *Synthesis* **2012**, *44*, 1491. (c) Jouvin, K.; Veillard, R.; Theunissen, C.; Alayrac, C.; Gaumont, A.-C.; Evano, G. *Org. Lett.* **2013**, *15*, 4592. (d) Theunissen, C.; Lecomte, M.; Jouvin, K.; Laouiti, A.; Guissart, C.; Heimburger, J.; Loire, E.; Evano, G. *Synthesis* **2014**, *46*, 1157. (e) Tresse, C.; Guissart, C.; Schweizer, S.; Bouhoute, Y.; Chany, A.-C.; Goddard, M.-L.; Blanchard, N.; Evano, G. *Adv. Synth. Catal.* **2014**, *356*, 2051. (f) Evano, G.; Jouvin, K.; Theunissen, C.; Guissart, C.; Laouiti, A.; Tresse, C.; Heimburger, J.; Bouhoute, Y.; Veillard, R.; Lecomte, M.; Nitelet, A.; Schweizer, S.; Blanchard, N.; Alayrac, C.; Gaumont, A.-C. *Chem. Commun.* **2014**, *50*, 10008.

(16) For general references on the oxidation of organocopper reagents, see: (a) Surry, D. S.; Spring, D. A. *Chem. Soc. Rev.* **2006**, *35*, 218. (b) Aves, S. J.; Spring, D. R. in *Patai Series: The Chemistry of Functional Groups. The Chemistry of Organocopper Compounds*, Vol. *24*, Rappoport, Z.; Marek, I., Eds., John Wiley & Sons Ltd, Chichester, 2009; pp 585−602.

(17) For the formation of carbon−carbon bonds by oxidation of organocuprates, see: (a) Lipshutz, B. H.; Siegmann, K.; Garcia, E.; Kayser, F. *J. Am. Chem. Soc.* **1993**, *115*, 9276. (b) Surry, D. S.; Su, X.; Fox, D. J.; Franckevicius, V.; Macdonald, S. J. F.; Spring, D. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 1870. (c) Surry, D. S.; Fox, D. J.; Macdonald, S. J. F.; Spring, D. R. *Chem. Commun.* **2005**, 2589. (d) Dubbaka, S. R.; Kienle, M.; Mayr, H.; Knochel, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 9093. (e) Aves, S. J.; Pike, K. G.; Spring, D. R. *Synlett* **2010**, 2839. For another area of the oxidative chemistry of organocopper reagents, the oxidation of vinylcopper species by oxenoids yielding to enolates, see: (f) Zhang, D.; Ready, J. M. *Org. Lett.* **2005**, *7*, 5681. (g) Minko, Y.; Pasco, M.; Lercher, L.; Botoshansky, M.; Marek, I. *Nature* **2012**, *490*, 522. (h) Minko, Y.; Pasco, M.; Lercher, L.; Marek, I. *Nat. Protoc.* **2013**, *4*, 749.

(18) Lu, L.; Yan, H.; Sun, P.; Zhu, Y.; Yang, H.; Liu, D.; Rong, G.; Mao, J. *Eur. J. Org. Chem.* **2012**, 1644.

(19) (a) Monguchi, D.; Yamamura, A.; Fujiwara, T.; Somete, T.; Mori, A. *Tetrahedron Lett.* **2010**, *51*, 850. (b) Li, Y.; Jin, J.; Qian, W.; Bao, W. *Org. Biomol. Chem.* **2010**, *8*, 326. (c) Zhu, M.; Fujita, K.-i.; Yamaguchi, R. *Chem. Commun.* **2011**, *47*, 12876.

(20) For recent review articles, see: (a) Boström, J.; Hogner, A.; Llinàs, A.; Wellner, E.; Plowright, A. T. *J. Med. Chem.* **2012**, *55*, 1814. (b) Khalilullah, H.; Ahsan, M. J.; Hedaitullah, M.; Khan, S.; Ahmed, B. *Mini-Rev. Med. Chem.* **2012**, *12*, 789. (c) Sun, J.; Makawana, J. A.; Zhu, H. L. *Mini-Rev. Med. Chem.* **2012**, *12*, 1725.

(21) For examples, see: (a) Mitschke, U.; Bäuerle, P. *J. Mater. Chem.* **2000**, *10*, 1471. (b) Jin, S.-H.; Kim, M.-Y.; Kim, J. Y.; Lee, K.; Gal, Y.-S. *J. Am. Chem. Soc.* **2004**, *126*, 2474. (c) He, G. S.; Tan, L.-S.; Zheng, Q.; Prasad, P. N. *Chem. Rev.* **2008**, *108*, 1245. (d) Tao, Y.; Wang, Q.; Yang, C.; Wang, Q.; Zhang, Z.; Zou, T.; Qin, J.; Ma, D. *Angew. Chem., Int. Ed.* **2008**, *47*, 8104.

(22) Shen, K.; Fu, Y.; Li, J.-N.; Liu, L.; Guo, Q.-X. *Tetrahedron* **2007**, *63*, 1568.

(23) For examples, see: (a) Babudri, F.; Colangiuli, D.; Di Lorenzo, P. A.; Farinola, G. M.; Hassan Omar, O.; Naso, F. *Chem. Commun.* **2003**, 130. (b) Babudri, F.; Farinola, G. M.; Naso, F.; Ragni, R. *Chem. Commun.* **2007**, 1003. (c) Dutta, T.; Woody, K. B.; Watson, M. D. *J. Am. Chem. Soc.* **2008**, *130*, 452.