Organic LETTERS

Letter

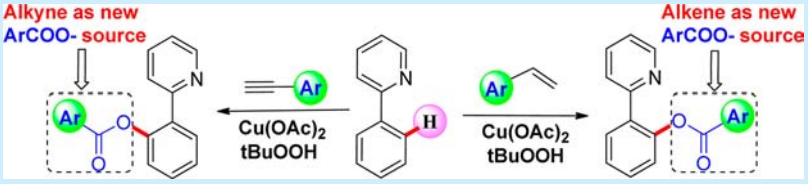
pubs.acs.org/OrgLett

Terminal Aryl Alkenes and Alkynes as Arylcarboxy Surrogates toward *o*-Benzoxylation of 2-Phenylpyridine Catalyzed by Copper

Saroj Kumar Rout,[†] Srimanta Guin,[†] Anupal Gogoi, Ganesh Majji, and Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology Guwahati, North Guwahati-781039, India

Supporting Information



ABSTRACT: A variety of styrenes and phenylacetylenes serve as excellent arylcarboxy sources in bringing about substrate directed *o*-benzoxylation of 2-phenylpyridine derivatives catalyzed by Cu(II) in the presence of TBHP. This reaction proceeds via formation of phenylglyoxal followed by decarbonylation to benzoyl radical/benzaldehyde which acts as the arylcarboxy source.

The combination of transition metal catalysts and chelation-assisted groups has brought about a renaissance in organic chemistry providing unprecedented results through selective functionalizations of unreactive *ortho* C−H bonds particularly for the construction of C−C and C−heteroatom bonds.[1] Thus C−H bond activation is one of the most alluring approaches in organic synthesis that obviates substrate prefunctionalization, thereby reducing the number of synthetic steps and making the method atom economic. Recently, our group has paid substantial attention to C−C and C−O bond formations via activation of sp^2 C−H and sp^3 C−H bonds[2,3] using a combination of transition metal catalysts and oxidants. Through sp^3 C−H activation, the inert alkylbenzenes have been found to be surrogates of $ArCH_2O-$,[3a] ArCO−,[3b,c] ArCOO−,[3e] and $ArCH_2-$[3e] equivalents.

Vinylations of substrates possessing directing groups have been successfully achieved using expensive metal catalysts such as Rh, Ru, and Pd.[4] Thus, it would be desirable and appreciable if the same can be achieved using less expensive and more environmentally benign metals such as Cu, albeit its use is so far unfamiliar in this forum. To check the efficacy of a copper catalyst toward radically induced *o*-alkenylation of 2-phenylpyridine (**1**) an initial reaction was performed using *p*-methoxy styrene (**e**) as the alkenyl source in the presence of $Cu(OAc)_2$ (10 mol %) and oxidant TBHP (3 equiv) in chlorobenzene at 100 °C (Table 1, entry 1). Instead of the expected *o*-alkenylated product the reaction interestingly provided *o*-benzoxylated product (**1e**) exclusively. This result is rather surprising as styrene is not known to be the synthetic equivalent for the benzoxy (ArCOO−) group. Related to the similar oxidation of alkenes, styrenes are reported to undergo Wacker type oxidation to give phenylacetaldehyde[5] while stilbenes are reported to yield 1,2-diketones.[6] Irrespective of the nature of the mechanism the current *o*-benzoxylation of 2-phenylpyridine (**1**) from styrene which is serving as ArCOO− surrogate via loss of one carbon atom is unprecedented in the literature.

Table 1. Screening of Reaction Conditions[a,b]

entry	catalyst (mol %)	oxidant[c] (equiv)	temp (°C)	yield (%)
1	$Cu(OAc)_2$ (10)	TBHP (3)	100	46
2	CuBr (10)	TBHP (3)	100	27
3	$CuBr_2$ (10)	TBHP (3)	100	21
4.	CuCl (10)	TBHP (3)	100	28
5.	$CuCl_2$ (10)	TBHP (3)	100	35
6.	$Cu(OTf)_2$ (10)	TBHP (3)	100	15
7	CuI (10)	TBHP (3)	100	33
8	$Cu(OAc)_2$ (10)	TBHP (4)	100	55
9	$Cu(OAc)_2$ (10)	TBHP (5)	100	62
10	$Cu(OAc)_2$ (20)	TBHP (5)	100	71
11	$Cu(OAc)_2$ (30)	TBHP (5)	100	72
12	**$Cu(OAc)_2$ (20)**	**TBHP (5)**	**120**	**78**

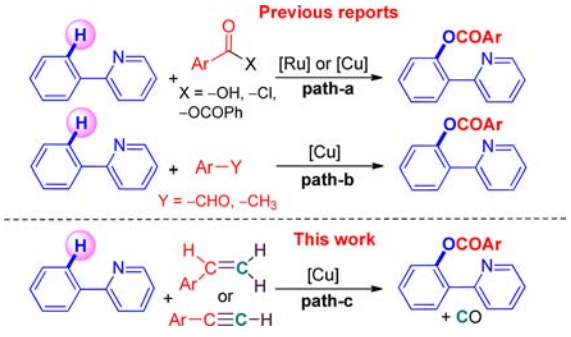
[a]Reaction conditions: 2-phenylpyridine (**1**) (0.5 mmol), *p*-methoxy styrene (**e**) (1 mmol), in chlorobenzene (1 mL), time 10 h. [b]Isolated yield. [c]Decane solution (5−6 M).

Acetoxylation[7] and hydroxylation[7d−f,8] are two common forms of C−O bond formation via C−H bond activation; however reports on benzoxylation are relatively fewer in numbers. Prior to this observation, *o*-benzoxylation of 2-phenylpyridine (**1**) has been achieved using benzoate iodonium salts by the Sanford group.[9] The same has been demonstrated using either the carboxylic acid/salt[10] or its derivatives such as anhydride,[11] acid chloride,[12] or peroxide[13] as the arylcarboxy sources using various metal catalysts (path-a, Scheme 1). Further, aldehyde (ArCHO) and alkylbenzene ($ArCH_3$) have been used as alternative sources of the ArCOO− group during *o*-benzoxylation of 2-phenylpyridine by Huang et al. (path-b, Scheme 1).[14] While for some other directing groups such as ketoxime ether[15] and acetanilides,[16] *o*-benzoxylation has been

Received: January 22, 2014
Published: March 3, 2014

 © 2014 American Chemical Society dx.doi.org/10.1021/ol500224e | *Org. Lett.* 2014, 16, 1614−1617

Scheme 1. Various Approaches to *o*-Benzoxylation

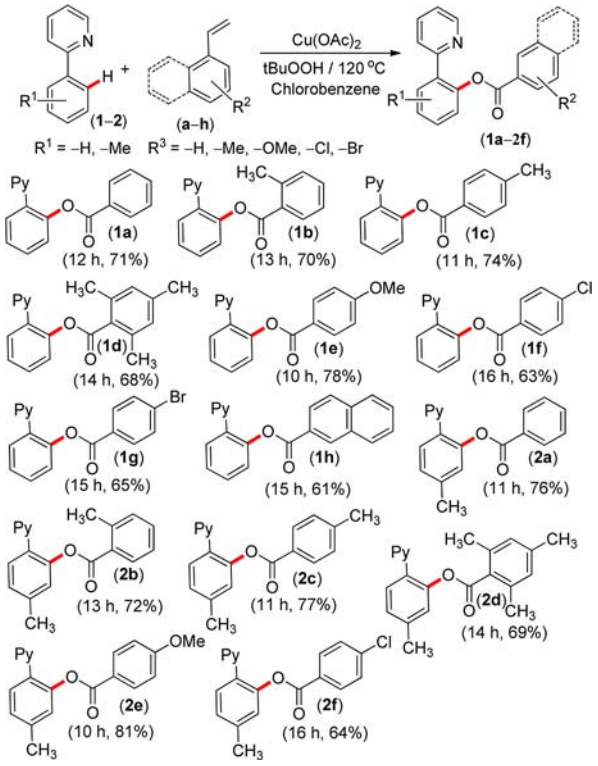


achieved using carboxylic acid in the presence of Pd and Ru catalysts respectively. Thus the present method using the Cu catalyst and styrene as the benzoxy surrogate is novel and unparalleled in the literature (path-c, Scheme 1).

Encouraged by this unique result, further optimizations were carried out to attain a better yield of the desired product. Among several catalysts screened, $Cu(OAc)_2$ (Table 1, entry 1) was found to be superior to various Cu(I) [CuBr, CuCl, and CuI] and Cu(II) [$CuBr_2$, $CuCl_2$, $Cu(OTf)_2$] salts (Table 1, entries 2–7). Subsequently by increasing the TBHP (5–6 M) quantity from 3 to 4 equiv, the product yield was enhanced to 55% (Table 1, entry 8) while a further improvement of 7% (Table 1, entry 9) was observed using 5 equiv of the same. The use of 6 equiv of TBHP did not make any further augmentation in the yield. A 2-fold increase in the catalyst loading led to a better yield (71%, Table 1, entry 10), while no significant change in yield occurred with a 3-fold excess of the catalyst loading. The yield was increased by an additional 7% (Table 1, entry 12) upon performing the reaction at 120 °C. Solvents toluene (68%) and THF (38%) were less efficient compared to the use of chlorobenzene (78%), whereas other solvents such as dioxane, DMSO, DMF, and DCE were completely ineffective in bringing about this transformation. The use of aq. TBHP in lieu of a decane solution of TBHP (5–6 M) was found to be far less effective giving only a 27% yield of the desired product under identical reaction conditions. The reaction failed to proceed in the absence of either the catalyst or the oxidant suggesting their combination as an essential requirement. Thus the use of $Cu(OAc)_2$ (20 mol %) and TBHP (5 equiv) in chlorobenzene at 120 °C was found to be the optimized conditions for our subsequent exploration to extend the scope of this transformation.

The above optimized conditions were then executed for *o*-benzoxylation of 2-phenylpyridine (**1**) using various substituted styrenes. The electron neutral −H (**a**) and electron-donating substituents on styrenes *viz*. *o*-Me (**b**), *p*-Me (**c**), 2,4,6-trimethyl (**d**), and *p*-OMe (**e**) served as excellent benzoxy surrogates toward *o*-benzoxylation of 2-phenylpyridine (**1**) providing their respective products (**1a**–**1e**) in moderate yields as shown in Scheme 2. Moderately electron-withdrawing substituents in styrenes such as *p*-Cl (**f**) and *p*-Br (**g**) also acted as their respective benzoxy sources yielding corresponding *o*-benzoxylated products (**1f** and **1g**) but in slightly lesser yields compared to styrenes possessing electron-donating substituents. However styrene possessing a strongly electron-withdrawing group such as *m*-NO_2 failed to give an *o*-benzoxylated product with **1**. The styrene analogue of naphthalene such as 2-vinylnaphthalene (**h**) were also effective in bringing about the naphthylcarboxylation of **1** giving **1h** in a

Scheme 2. Substrate Scope for *o*-Benzoxylation[a,b]



[a]Reaction conditions: arenes (**1**–**2**) (0.5 mmol), alkenes (**a**–**h**) (1 mmol), $Cu(OAc)_2$ (0.1 mmol), TBHP (5–6 M) (5 mmol), 120 °C, in chlorobenzene (1 mL), time 10–16 h. [b] Yield of isolated pure product.

moderate yield. In addition to **1**, *o*-benzoxylation of 2-(*p*-tolyl)pyridine (**2**) was also investigated with various styrenes and the results are depicted in Scheme 2. The trends in the reactivity of substituted styrenes were found to be identical to those observed for **1**. Nevertheless, the yields of the *o*-benzoxylated products (**2a**–**2f**) obtained were marginally better with **2** than **1**, which is perhaps due to better chelation of the metal catalyst with the electron-rich *o*-tolyl ring in **2**. Surprisingly, terminal aliphatic alkene 1-methyl 4-butene failed to undergo any *o*-acetoxylation with either **1** or **2** under the present reaction conditions.

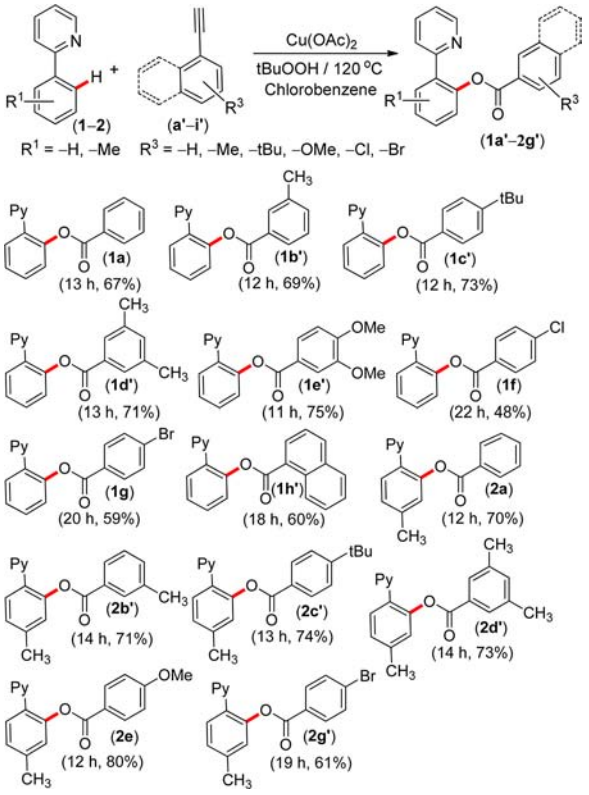
Terminal alkynes have been used for the alkynylation of sp^2 and sp^3 C–H bonds via metal catalyzed cross dehydrogenative coupling (CDC).[11,17] Specifically in the directing group-assisted C–H activation process, phenylacetylenes are reported to undergo regio- and/or stereoselective alkenylation.[17c] To explore their utility in C–H activation processes we intended to investigate whether phenylacetylene (**a′**) can act as a possible alkynyl source or as a benzoxy surrogate similar to styrene. Thus, **1** and **a′** were reacted in the presence of $Cu(OAc)_2$ and TBHP under the aforementioned reaction conditions. To our surprise and delight the product was again found to be *o*-benzoxylated product **1a** obtained in a moderate yield of 67%. This is yet another noteworthy observation where **a′** is found to be the benzoxy surrogate (path-c, Scheme 1).

To check the practicality of this methodology a set of arylalkynes having electron-donating groups such as *m*-Me (**b′**), *p*-tBu (**c′**), 3,5-diMe (**d′**), and 3,4-diOMe (**e′**) were investigated as the potential benzoxy sources for the *o*-benzoxylation of **1**. Each of these alkynes (**b′**–**e′**) served as excellent surrogates of the benzoxy group providing *o*-

dx.doi.org/10.1021/ol500224e | *Org. Lett.* 2014, 16, 1614–1617

benzoxylated products (**1b′**−**1e′**) in moderate yields (Scheme 3). Alkynes possessing electron-withdrawing substituents such

Scheme 3. Substrate Scope for *o*-Benzoxylation[a,b]



[a]Reaction conditions: arenes (**1**−**2**) (0.5 mmol), alkynes (**a′**−**i′**) (1 mmol), $Cu(OAc)_2$ (0.1 mmol), TBHP (5 mmol), 120 °C, in chlorobenzene (1 mL), time 11−22 h. [b] Yield of isolated pure product.

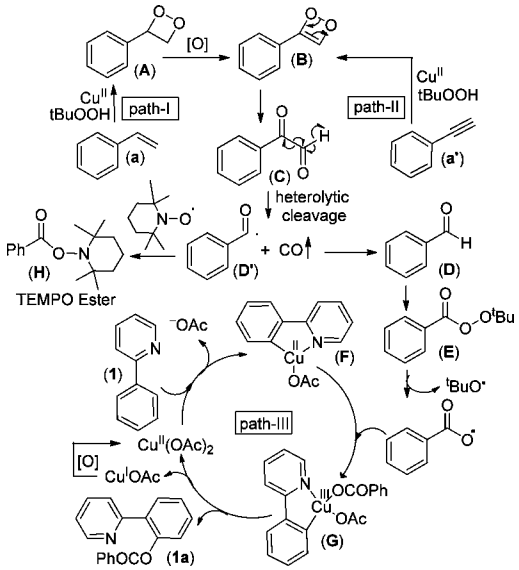
as *p*-Cl (**f′**) and *p*-Br (**g′**) when treated with **1** gave *o*-benzoxylated products **1f** and **1g** in 48% and 59% yields respectively. *o*-Naphthylcarboxylation (**1h′**) was achieved successfully in 60% yield using 1-naphthylalkyne (**h′**) as the benzoxy counterpart. The yields of the products obtained using substituted phenylacetylenes followed similar trends as those with substituted styrenes.

As in the case of **1**, *o*-benzoxylation of **2** was achieved successfully using unsubstituted or substituted phenylacetylenes. Treatment of **2** with **a′** under the present reaction conditions gave *o*-benzoxylated product **2a** in 70% isolated yield. For substituted phenylacetylenes possessing electron-donating *m*-Me (**b′**), *p*-tBu (**c′**), 3,5-diMe (**d′**), and *p*-OMe (**i′**) and electron-withdrawing group *p*-Br (**g′**), their reactivity and yield trends were found to be similar to those from their reactions with **1** as shown in Scheme 3.

This elegant and unprecedented transformation is a mechanistic enigma to us, and hence systematic investigations were carried out to depict a plausible mechanism. Two possible intermediates, viz. styrene epoxide and 1-phenyl-1,2-ethanediol, could be generated in the reaction medium when styrene (**a**) is treated in the presence of Cu/TBHP. So in lieu of styrene two independent reactions were performed, one with styrene epoxide and the other using 1-phenyl-1,2-ethanediol, but both reactions failed to offer the expected product (**1a**), thus ruling out the involvement of either of them as possible intermediates. A careful examination of the reaction mixture obtained by reacting **1** with **a** divulges the presence of intermediates such as phenylglyoxal, benzaldehyde, and benzoic acid in the medium. Surprisingly instead of styrene any one of these intermediates provided the desired product (**1a**). Under the oxidative conditions, the conversion of benzaldehyde to benzoic acid is not surprising but the formation of phenylglyoxal from styrene and a further loss of one C-atom to form benzaldehyde (possibly from phenylglyoxal) were rather puzzling. The detection of CO in the reaction mixture accounts for the loss of one carbon possibly from phenylglyoxal. In a control experiment when phenylglyoxal was treated under the identical reaction conditions, detection of CO and formation of benzaldehyde were observed reconfirming our assumption (see Supporting Information (SI)).[18] This reaction is most probably proceeding via a radical mechanism. To ascertain this, a reaction was performed in the presence of radical quencher TEMPO. Substantial rate retardation giving only traces of desired product **1a** and isolation of TEMPO ester (**H**) confirms our presumption (Scheme S1, SI). The observed intermediates were identical even when **a′** was used instead of **a** suggesting the identical reaction path and mechanism leading to *o*-benzoxylation.

Parallel to the observations of the above-mentioned experiments a mechanism is proposed composed of three paths as shown in Scheme 4. In path-I, styrene (**a**) possibly forms a

Scheme 4. Proposed Mechanism for *ortho*-Benzoxylation



four-membered cyclic intermediate, 3-phenyl-1,2-dioxetane (**A**), upon reaction with TBHP. Intermediate **A** then undergoes oxidative dehydrogenation to generate intermediate 3-phenyl-1,2-dioxete (**B**). The formation of similar intermediates under oxidative conditions has been proposed by Jiao et al.[19] On the other hand, phenylacetylene (**a′**) upon reaction with oxidant TBHP affords the same intermediate (**B**) directly (path-II, Scheme 4). The ring fragmentation of **B** provides phenylglyoxal (**C**) which ultimately heads to the formation of benzaldehyde (**D**) via a benzoyl radical (**D′**) through radically induced decarbonylation. The effect of TBHP on **D** or **D′** forms *tert*-butyl benzoperoxate (**E**). In path-III, Cu(II) undergoes chelation with **1** to give the complex **F**. Loss of the ^{t}BuO radical from **E** with subsequent ligation of the benzoxy radical with **F** gives the Cu(III) intermediate **G**. Successful

dx.doi.org/10.1021/ol500224e | *Org. Lett.* 2014, 16, 1614−1617

benzoxylation of **1** using either **D** or presynthesized **E** under identical reaction conditions supports their intermediacy in this transformation. The reductive elimination in the final step leads to the *o*-benzoxylated product **1a** while the Cu(I) generated is reoxidized to Cu(II) for the next catalytic cycle.

In conclusion, this methodology illustrates the use of styrenes and phenylacetylenes as the new surrogates for the arylcarboxy group (ArCOO−), which has been employed intriguingly for the *o*-benzoxylation of 2-phenylpyridine derivatives. Based on the reaction intermediates detected, a plausible mechanism has been proposed which accounts for most of the experimental observations.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details, spectral and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: patel@iitg.ernet.in.

Author Contributions

†These authors contributed equally.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

B.K.P. acknowledges the support of this research by the Department of Science and Technology (DST) (SB/S1/OC-53/2013), New Delhi, and the Council of Scientific and Industrial Research (CSIR) (02(0096)/12/EMR-II). S.G. and S.K.R. thank CSIR.

■ DEDICATION

This manuscript is dedicated to Prof. Bijay Kumar Mishra on the occasion of his 60th Birthday.

■ REFERENCES

(1) (a) Dyker, G. *Handbook of C−H Transformations: Applications in Organic Synthesis*; Wiley-VCH: Weinheim, 2005. (b) Yu, J.-Q.; Shi, Z.-J. *C−H Activation*; Springer: Berlin, Germany, 2010. (c) Satoh, T.; Miura, M. *Chem.—Eur. J.* **2010**, *16*, 11212. (d) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2009**, *48*, 5094. (e) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (f) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712. (g) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (h) Wencel-Delord, J.; Droge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740. (i) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. *Chem. Soc. Rev.* **2011**, *40*, 5068. (j) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293. (k) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315. (l) Girard, A. S.; Knauber, T.; Li, C. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 2. (m) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R.; Kozlowski, M. C. *Chem. Rev.* **2013**, *113*, 6234.

(2) (a) Guin, S.; Ghosh, S.; Rout, S. K.; Banerjee, A.; Patel, B. K. *Org. Lett.* **2011**, *13*, 5976. (b) Sahoo, S. K.; Banerjee, A.; Chakraborty, S.; Patel, B. K. *ACS Catal.* **2012**, *2*, 544. (c) Banerjee, A.; Santra, S. K.; Guin, S.; Rout, S. K.; Patel, B. K. *Eur. J. Org. Chem.* **2012**, 1376. (d) Banerjee, A.; Bera, A.; Guin, S.; Rout, S. K.; Patel, B. K. *Tetrahedron* **2013**, *69*, 2175. (e) Banerjee, A.; Santra, S. K.; Rout, S. K.; Patel, B. K. *Tetrahedron.* **2013**, *69*, 9096.

(3) (a) Rout, S. K.; Guin, S.; Ghara, K. K.; Banerjee, A.; Patel, B. K. *Org. Lett.* **2012**, *14*, 3982. (b) Guin, S.; Rout, S. K.; Banerjee, A.; Nandi, S.; Patel, B. K. *Org. Lett.* **2012**, *14*, 5294. (c) Rout, S. K.; Guin, S.; Banerjee, A.; Khatun, N.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2013**, *15*, 4106. (d) Gogoi, A.; Guin, S.; Rout, S. K.; Patel, B. K. *Org. Lett.* **2013**, *15*, 1802. (e) Majji, G.; Guin, S.; Gogoi, A.; Rout, S. K.; Patel, B. K. *Chem. Commun.* **2013**, *49*, 3031.

(4) (a) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (b) Beccalli, E. M.; Broggini, G.; Martinelli, M.; Sottocornola, S. *Chem. Rev.* **2007**, *107*, 5318. (c) Bras, J. L.; Muzart, J. *Chem. Rev.* **2011**, *111*, 1170. (d) Yeung, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215.

(5) Teo, P.; Wickens, K. Z.; Dong, G.; Grubbs, H. R. *Org. Lett.* **2012**, *14*, 3237.

(6) Chen, S.; Liu, Z.; Shi, E.; Chen, L.; Wei, W.; Li, H.; Cheng, Y.; Wan, X. *Org. Lett.* **2011**, *13*, 2274.

(7) (a) Kalyani, D.; Sanford, M. S. *Org. Lett.* **2005**, *7*, 4149. (b) Gou, F.-R.; Wang, X.-C.; Huo, P.-F.; Bi, H.-P.; Guan, Z.-H.; Liang, Y.-M. *Org. Lett.* **2009**, *11*, 5726. (c) Zheng, X.; Song, B.; Xu, B. *Eur. J. Org. Chem.* **2010**, 4376. (d) Wang, L.; Xia, X.-D.; Guo, W.; Chen, J.-R.; Xiao, W.-J. *Org. Biomol. Chem.* **2011**, *9*, 6895. (e) Rit, R. K.; Yadav, R.; Sahoo, A. K. *Org. Lett.* **2012**, *14*, 3724. (f) Yadav, R.; Rit, R. K.; Sahoo, A. K. *Chem.—Eur. J.* **2012**, *18*, 5541.

(8) (a) Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790. (b) Kim, S. H.; Lee, H. S.; Kim, S. H.; Kim, J. N. *Tetrahedron Lett.* **2008**, *49*, 5863. (c) Company, A.; Enthaler, S. *Chem. Soc. Rev.* **2011**, *40*, 4912. (d) Alonso, D. A.; Najera, C.; Pastor, I. M.; Yus, M. *Chem.—Eur. J.* **2010**, *16*, 5274. (e) Thirunavukkarasu, V. S.; Kozhushkov, S. I.; Ackermann, L. *Chem. Commun.* **2014**, *50*, 29.

(9) Dick, R. A.; Kampf, W. J.; Sanford, S. M. *J. Am. Chem. Soc.* **2005**, *127*, 12790.

(10) (a) Ye, Z.; Wang, W.; Luo, F.; Zhang, S.; Cheng, J. *Org. Lett.* **2009**, *11*, 3974. (b) Hu, C.-J.; Zhang, X.-H.; Ding, Q.-P.; Lv, T.; Ge, S.-P.; Zhong, P. *Tetrahedron Lett.* **2012**, *53*, 2465. (c) Liping, L.; Peng, Y.; Jiang, C.; Fan, C.; Changduo, P. *Chem. Lett.* **2012**, *41*, 600.

(11) Wang, W.; Luo, F.; Zhang, S.; Cheng, J. *J. Org. Chem.* **2010**, *75*, 2415.

(12) Wang, W.; Pan, C.; Chen, F.; Cheng, J. *Chem. Commun.* **2011**, *47*, 3978.

(13) Sit, W. N.; Chan, C. W.; Yu, W. Y. *Molecules* **2013**, 18.

(14) Bian, Y.-J.; Xiang, C.-B.; Chen, Z.-M.; Huang, Z.-Z. *Synlett* **2011**, *16*, 2407.

(15) Sun, C.-L.; Liu, J.; Wang, Y.; Zhou, X.; Li, B.-J.; Shi, Z.-J. *Synlett* **2011**, *7*, 883.

(16) Padala, K.; Jeganmohan, M. *Chem. Commun.* **2013**, *49*, 9651.

(17) (a) Kakiuchi, F.; Yamamoto, Y.; Chatani, N.; Murai, S. *Chem. Lett.* **1995**, 681. (b) Lim, Y.-G.; Lee, K.-H.; Koo, B. T.; Kang, J.-B. *Tetrahedron Lett.* **2001**, *42*, 7609. (c) Cheng, K.; Yao, B.; Zhao, J.; Zhang, Y. *Org. Lett.* **2008**, *10*, 5309. (d) Zhou, B.; Chen, H.; Wang, C. *J. Am. Chem. Soc.* **2013**, *135*, 1264. (e) Johnson, G. D.; Lynam, M. J.; Mistry, S. N.; Slattery, M. J.; Thatcher, J. R.; Whitwood, C. A. *J. Am. Chem. Soc.* **2013**, *135*, 2222.

(18) (a) Feigl, F.; Anger, V. *Spot Tests in Inorganic Analysis*, 6th ed.; Elsevier: 1988; p 169. (b) Wang, L.; Ren, X.; Yu, J.; Jiang, Y.; Cheng, J. *J. Org. Chem.* **2013**, *78*, 12076.

(19) Zhang, C.; Jiao, N. *J. Am. Chem. Soc.* **2010**, *132*, 28.