Cross-Coupling Reactions

Deutsche Ausgabe: DOI: 10.1002/ange.201501287
Internationale Ausgabe: DOI: 10.1002/anie.201501287

Copper-Catalyzed Radical/Radical C_{sp^3}–H/P–H Cross-Coupling: α-Phosphorylation of Aryl Ketone *O*-Acetyloximes[**]

*Jie Ke, Yuliang Tang, Hong Yi, Yali Li, Yongde Cheng, Chao Liu, and Aiwen Lei**

Abstract: *The selective radical/radical cross-coupling of two different organic radicals is a great challenge due to the inherent activity of radicals. In this paper, a copper-catalyzed radical/radical C_{sp^3}–H/P–H cross-coupling has been developed. It provides a radical/radical cross-coupling in a selective manner. This work offers a simple way toward β-ketophosphonates by oxidative coupling of aryl ketone o-acetyloximes with phosphine oxides using CuCl as catalyst and PCy_3 as ligand in dioxane under N_2 atmosphere at 130°C for 5 h, and yields ranging from 47% to 86%. The preliminary mechanistic studies by electron paramagnetic resonance (EPR) showed that, 1) the reduction of ketone o-acetyloximes generates iminium radicals, which could isomerize to α-sp^3-carbon radical species; 2) phosphorus radicals were generated from the oxidation of phosphine oxides. Various aryl ketone o-acetyloximes and phosphine oxides were suitable for this transformation.*

C–P bond formation is of great importance in organic synthesis because phosphorus-containing compounds have wide applications in organic chemistry,[1] medicinal chemistry,[2] and material chemistry.[3] Along with the development of transition-metal-catalyzed oxidative cross-coupling reactions,[4] more and more attention was paid to the studies of C–P bond construction by oxidative cross-coupling between C–H and P–H bonds. Although some progress has been made in this emerging field,[5] there still remains a great challenge in oxidative C_{sp^3}–H/P–H cross-coupling,[6] especially the direct ketone α-C_{sp^3}–H/P–H coupling. This may be due to the nucleophilic addition of phosphorus to the carbonyl compound.[7] Recently, radical processes have been receiving special attention in the first-row transition-metal-catalyzed and photocatalytic oxidative cross-coupling.[8] It is known that the phosphorus radical could also be generated from the oxidation of H-phosphonate.[5b,c,d,9] We wondered whether a radical/radical cross-coupling phosphorylation strategy in oxidative C_{sp^3}–H/P–H coupling could be developed to allow the C_{sp^3}–P bond formation with more alternatives.

It was widely believed that the direct coupling of two radicals would represent a powerful approach for bond formations.[10] However, most radicals are so reactive that it is hard to achieve the selective cross-coupling of two different radicals, which limits the application of this protocol in organic synthesis. Usually, the selective radical/radical cross-coupling is based on the Ingold–Fischer "persistent radical effect". Only the radical coupling between a persistent radical and a transient radical would lead to a selective bond formation.[11] In general terms, an sp^3-carbon-centered radical without steric hindrance and conjugation effect can be regarded as a transient radical due to the short half-life. Although a phosphorus radical generated from diaryl phosphine oxide exhibits large steric hindrance, it may be considered as a persistent radical.[11a] If methods could be developed to generate α-ketone carbon radicals and phosphorus radicals from α-C_{sp^3}–H and H-phosphonate in the same system, C_{sp^3}–P bond formation might be realized through selective radical/radical cross-coupling.

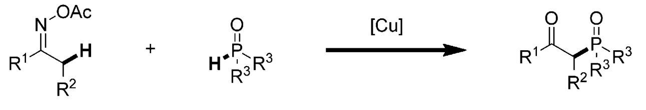
Reactions that use an internal oxidant are redox neutral, thus, excess external oxidants could be avoided. Ketone *o*-acetyloxime is a kind of internal oxidant, which can be easily prepared by the reaction of ketone, hydroxylamine hydrochloride, and acetic anhydride under mild conditions.[12] Therefore, it has been widely used for the development of transition-metal-catalyzed α-C_{sp^3}–H bond activation reactions.[13] We proposed that the reduction of an aryl ketone *o*-acetyloxime by Cu^I may afford an iminium radical intermediate which could isomerize to an α-carbon radical species (transient radical).[14] On the other hand, oxidation of phosphine oxides by Cu^{II} may generate the phosphorus radical (persistent radical). Subsequently, selective cross-coupling of this two radicals can lead to the formation of β-ketophosphonates (Schemes 1 and 3), which are valuable commodity chemicals in organic chemistry, especially for the construction of α,β-unsaturated carbonyl compounds through

---

[*] J. Ke, Y. Tang, H. Yi, Y. Cheng, C. Liu, Prof. A. Lei
College of Chemistry and Molecular Sciences
The Institute for Advanced Studies (IAS), Wuhan University
Wuhan, Hubei 430072 (P.R. China)
E-mail: aiwenlei@whu.edu.cn
Homepage: http://aiwenlei.whu.edu.cn/Main_Website/
Prof. A. Lei
State Key Laboratory for Oxo Synthesis and Selective Oxidation
Lanzhou Institute of Chemical Physics
730000 Lanzhou (P.R. China)
Y. Li
Key Laboratory for Organic Electronics and Information Display and Institute of Advanced Materials, Nanjing University of Posts and Telecommunications
Nanjing, 210023 (P.R. China)

[**] This work was supported by the 973 Program (2012CB725302, 2011CB808600), the National Natural Science Foundation of China (21390400, 21272180, and 21302148), the Research Fund for the Doctoral Program of Higher Education of China (20120141130002), the Program for Changjiang Scholars and Innovative Research Team in University (IRT1030), and the Ministry of Science and Technology of China (2012YQ120060). The Program of Introducing Talents of Discipline to Universities of China (111 Program) is also acknowledged. Particular thanks also go Prof. Longmin Wu for his guidance in EPR experiments.

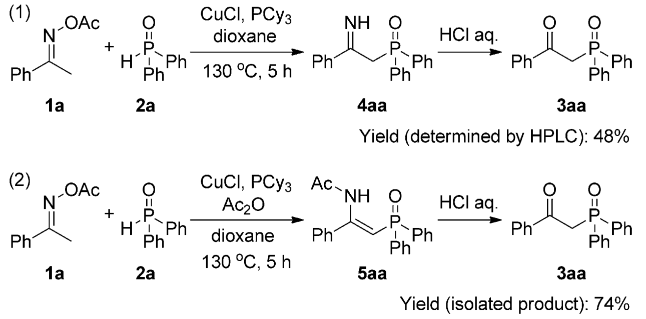
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201501287.



Scheme 1. Proposed strategy for the cross-coupling of aryl ketone *o*-acetyloximes with phosphine oxides.

the well-known Horner–Wadsworth–Emmons (HWE) reaction.[1a,b]

Our initial efforts focused on the reaction of acetophenone oxime acetate **1a** with diphenylphosphine oxide **2a** using CuCl as the catalyst precursor and PCy_3 as the ligand. To our delight, when the mixture in dioxane was heated at 130 °C for 5 h, the desired product **4aa** was detected by LC-MS. It was hydrolyzed by diluted hydrochloric acid (HCl aq.) to afford β-ketophosphonate **3aa** in 48 % yield (Scheme 2 (1)). As we know, most of the radical/radical cross-coupling reactions are reversible. Converting **4aa** to the more stable compound may shift the equilibrium toward the final product. Therefore, acetic anhydride (Ac_2O) was chosen as an additive. Indeed, in the presence of Ac_2O, the yield of **3aa** increased to 74 %. Without hydrolysis by aqueous HCl, a diphenylphosphoryl enamine product **5aa** was isolated in 71 % yield, which may result from the reaction of **4aa** with Ac_2O (Scheme 2 (2)). Finally, a control reaction demonstrated that only 16 % yield of the final product **3aa** was obtained in the absence of copper catalyst (for more details see the Supporting Information (SI), Table S1).



Scheme 2. Copper-catalyzed oxidative cross-coupling of **1a** with **2a**. Conditions: 1) **1a** (0.5 mmol), **2a** (0.6 mmol), CuCl (0.1 mmol), PCy_3 (0.1 mmol), dioxane (2.0 mL), 130 °C, 5 h, under N_2. 2) **1a** (0.5 mmol), **2a** (0.6 mmol), CuCl (0.1 mmol), PCy_3 (0.1 mmol), Ac_2O (0.5 mmol), dioxane (2.0 mL), 130 °C, 5 h, under N_2.

To confirm our hypothesis for this oxidative C_{sp^3}–H/P–H coupling reaction undergoing a radical/radical cross-coupling process, a series of mechanistic studies by electron paramagnetic resonance (EPR) spectroscopy was performed. Firstly, the valence state of the copper species was determined by EPR. An EPR signal of a Cu^{II} species was observed in the stoichiometric reaction of **1a**, CuCl, and PCy_3 (Figure 1 a). When the free-radical spin-trapping agent DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) was added to the reaction, a signal of the trapping radical was observed (Figure 1 a, in the box). Enlargement of this signal is shown in Figure 1 b. Data analysis suggests that a nitrogen radical is generated and quickly trapped by DMPO to form the relatively stable radical **A** ($g = 2.0059$, $a_{N1} = 13.68$ G, $a_H = 13.68$ G, $a_{N2} = 2.84$ G). These results illustrated that aryl ketone *o*-acetyloxime can oxidize Cu^I to Cu^{II} species, while it is reduced to an iminium radical.

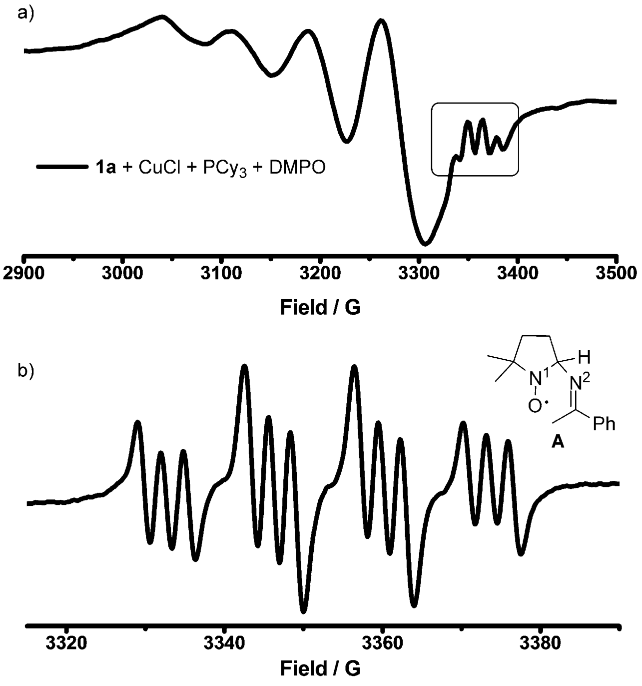


Figure 1. The electron paramagnetic resonance (EPR) spectra (*X* band, 9.4 GHz, room temperature) of the reaction mixture of **1a**, CuCl, and PCy_3 in dioxane at 130 °C.

Further EPR experiments were performed to detect the phosphorus radical intermediate with the addition of free radical spin trapping agent MNP (2-methyl-2-nitrosopropane). To our delight, when MNP was added to the stoichiometric reaction of **1a**, CuCl, PCy_3, Ac_2O, and **2a**, an EPR signal was identified (Figure 2). Data analysis suggest that phosphorus radical generated and quickly trapped by MNP to form the relatively stable radical **B** ($a_N = 10.54$ G, $a_P = 11.76$ G).[15]

On the basis of the above results and previous studies, we proposed a radical/radical cross-coupling pathway for this

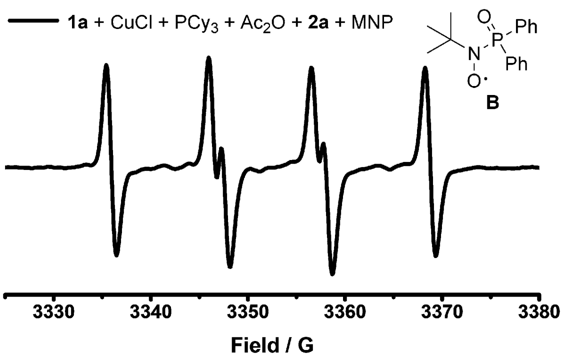
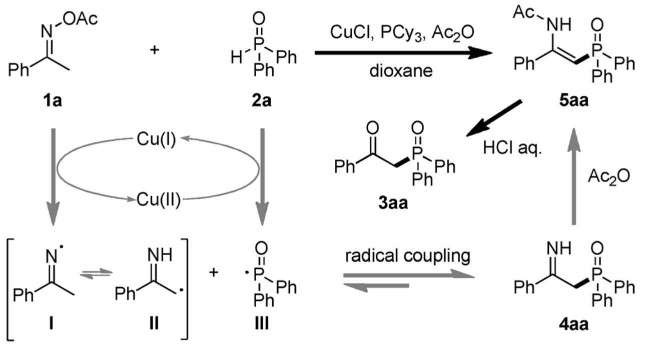


Figure 2. The electron paramagnetic resonance (EPR) spectra (*X* band, 9.4 GHz, room temperature) of the reaction mixture of **1a**, CuCl, PCy_3, Ac_2O, and **2a** in dioxane at 130 °C.

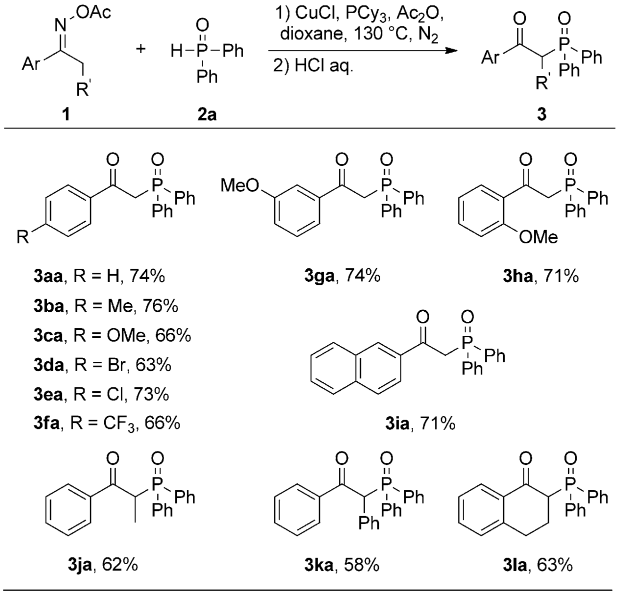


Scheme 3. Putative mechanism.

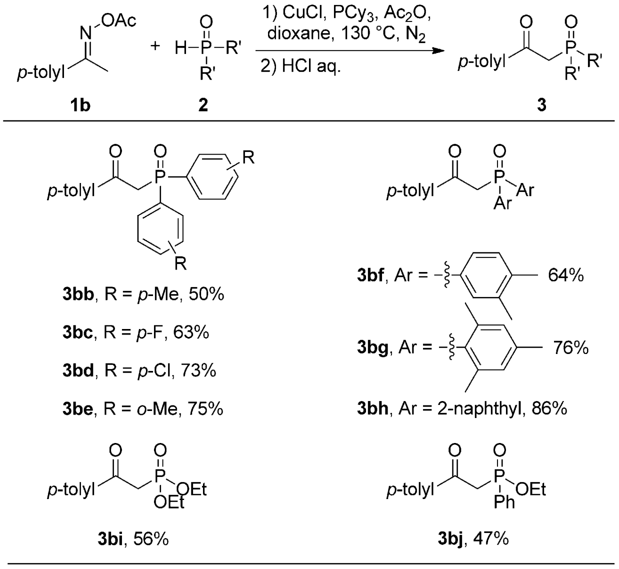
copper-catalyzed oxidative phosphorylation reaction (Scheme 3). Firstly, reduction of **1a** by Cu^{I} affords iminium radical **I**, which may quickly isomerize to α-carbon radical **II**. On the other hand, oxidation of diphenylphosphine oxide **2a** by Cu^{II} generates the phosphorus radical **III**. Next, selective cross-coupling of the radical species **II** and **III** constructed a new C–P bond to afford **4aa**. This radical/radical cross-coupling may be a reversible reaction. A relatively stable compound **5aa** was generated by a substitution reaction of **4aa** with Ac_2O, which shifted the equilibrium toward the desired reaction product. Final product **3aa** was obtained by hydrolysis of **5aa**.

With these insights into the mechanism and the optimized reaction conditions, we next explored the substrate scope of this copper-catalyzed oxidative phosphorylation reaction. Firstly, various aryl ketone *o*-acetyloximes **1** were coupled with diphenylphosphine oxide **2a** under the standard conditions (Scheme 4). Aryl ketone *o*-acetyloximes with electron-rich substituents (*p*-Me, *p*-OMe) or electron-poor substituent (*p*-CF_3), as well as the *ortho*-, *meta*-, and *para*-substituted groups all gave the desired products in satisfactory yields (**3ba**–**3ca**, **3fa**–**3ha**). Halogen substituents such as bromine and chlorine were well tolerated, affording the corresponding products in 63 % and 73 % yield, respectively (**3da**–**3ea**). Naphthalen-2-yl ethanone oxime acetates is also a suitable substrate for this reaction (**3ia**). It is noteworthy that propiophenone, 1,2-diphenylethanone, and 3,4-dihydronaphthalen-1(2*H*)-one oxime acetates also gave good yields of the desired β-ketophosphonates (**3ja**–**3la**).

We further examined the scope of phosphine oxides **2** using **1b** as the coupling partner and the results are listed in Scheme 5. Both electron-donating and electron-withdrawing substituents on the aryl groups were well tolerated in this reaction (**3bb**–**3bd**) and the *o*-methyl substituted substrate afforded a higher yield of 75 % (**3be**). In addition, substrates bearing multiple substituents also worked well (**3bf**, **3bg**) and di-2-naphthylphosphine oxide could also deliver the desired product **3bh** with a good yield of 86 %. Moreover, diethyl phosphonate and ethyl phenylphosphinate could also afford the corresponding β-ketophosphonates in moderate yields (**3bi**, **3bj**).



Scheme 4. Substrate scope for the copper-catalyzed oxidative phosphorylation of **2a** with aryl ketone *O*-acetyloximes **1**. Conditions: **1** (0.5 mmol), **2a** (0.6 mmol), CuCl (0.1 mmol), PCy_3 (0.1 mmol), Ac_2O (0.5 mmol), dioxane (2.0 mL), 130 °C, 5 h, under N_2. Yields are of isolated products.



Scheme 5. Substrate scope for the copper-catalyzed oxidative phosphorylation of phosphine oxides **2** with **1b**. Conditions: **1b** (0.5 mmol), **2** (0.6 mmol), CuCl (0.1 mmol), PCy_3 (0.1 mmol), Ac_2O (0.5 mmol), dioxane (2.0 mL), 130 °C, 5 h, under N_2. Yields are of isolated products.

In conclusion, we have disclosed a copper-catalyzed radical/radical cross-coupling reaction. This transformation offered a new protocol for C_{sp^3}–P bond formation by direct oxidative C_{sp^3}–H/P–H coupling. During the reaction, an α-C_{sp^3} radical species (transient radical) and a phosphorus radical species (persistent radical) were generated in the same system by using an internal oxidant. The cross-coupling of the two radical species is selective based on the "persistent radical effect". Various aryl ketone *o*-acetyloximes and phosphine oxides were suitable for this transformation. The application of this powerful strategy to other radical/radical cross-coupling reactions with various persistent radicals and further mechanistic investigations are underway in our laboratory.

Experimental Section

General procedure: a mixture of acetophenone oxime acetate **1a** (0.5 mmol), diphenylphosphine oxide **2a** (0.6 mmol), CuCl (0.1 mmol, 20 mol %), PCy_3 (0.1 mmol, 20 mol %), and Ac_2O (0.5 mmol) in dioxane (2 mL) was stirred under N_2 at 130 °C for 5 h. After completion of the reaction, as indicated by TCL, it was quenched by diluted hydrochloride (4 mL, 2 M). The mixture was extracted with diethyl ether and the organic phase was washed with aqueous K_2CO_3 and brine, and dried over Na_2SO_4. The pure product was obtained by flash column chromatography on silica gel (ethyl acetate). The desired product was isolated as a white solid in 74 % yield. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.02$–7.94 (m, 2 H), 7.86–7.75 (m, 4 H), 7.56–7.36 (m, 9 H), 4.15 ppm (d, $J = 15.2$ Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$): $\delta = 193.0$ (d, $J = 5.7$ Hz), 137.1, 133.8, 132.4 (d, $J = 2.7$ Hz), 132.1 (d, $J = 103.7$ Hz), 131.3 (d, $J = 9.9$ Hz), 129.4, 128.9, 128.8, 128.7, 43.5 ppm (d, $J = 58.2$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 27.18$ ppm.

Keywords: C(sp^3)—P bonds · copper catalysis · oxidative coupling · radical/radical cross-coupling · β-ketophosphonates

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 6604–6607
Angew. Chem. **2015**, *127*, 6704–6707

---

[1] a) J. Boutagy, R. Thomas, *Chem. Rev.* **1974**, *74*, 87–99; b) B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* **1989**, *89*, 863–927; c) M. Kitamura, M. Tokunaga, R. Noyori, *J. Am. Chem. Soc.* **1995**, *117*, 2931–2932.

[2] a) M. Sawa, T. Kiyoi, K. Kurokawa, H. Kumihara, M. Yamamoto, T. Miyasaka, Y. Ito, R. Hirayama, T. Inoue, Y. Kirii, E. Nishiwaki, H. Ohmoto, Y. Maeda, E. Ishibushi, Y. Inoue, K. Yoshino, H. Kondo, *J. Med. Chem.* **2002**, *45*, 919–929; b) X. Chen, D. J. Kopecky, J. Mihalic, S. Jeffries, X. Min, J. Heath, J. Deignan, S. Lai, Z. Fu, C. Guimaraes, S. Shen, S. Li, S. Johnstone, S. Thibault, H. Xu, M. Cardozo, W. Shen, N. Walker, F. Kayser, Z. Wang, *J. Med. Chem.* **2012**, *55*, 3837–3851.

[3] a) H. R. Allcock, M. A. Hofmann, C. M. Ambler, R. V. Morford, *Macromolecules* **2002**, *35*, 3484–3489; b) H. Onouchi, T. Miyagawa, A. Furuko, K. Maeda, E. Yashima, *J. Am. Chem. Soc.* **2005**, *127*, 2960–2965; c) C. Queffélec, M. Petit, P. Janvier, D. A. Knight, B. Bujoli, *Chem. Rev.* **2012**, *112*, 3777–3807.

[4] a) C. Jia, T. Kitamura, Y. Fujiwara, *Acc. Chem. Res.* **2001**, *34*, 633–639; b) M. Miura, M. Nomura, *Top. Curr. Chem.* **2002**, *219*, 211–241; c) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077–1101; d) D. Alberico, M. E. Scott, M. Lautens, *Chem. Rev.* **2007**, *107*, 174–238; e) X. Chen, K. M. Engle, D.-H. Wang, J.-Q. Yu, *Angew. Chem. Int. Ed.* **2009**, *48*, 5094–5115; *Angew. Chem.* **2009**, *121*, 5196–5217; f) O. Daugulis, H.-Q. Do, D. Shabashov, *Acc. Chem. Res.* **2009**, *42*, 1074–1086; g) C.-J. Li, *Acc. Chem. Res.* **2009**, *42*, 335–344; h) G. P. McGlacken, L. M. Bateman, *Chem. Soc. Rev.* **2009**, *38*, 2447–2464; i) J. A. Ashenhurst, *Chem. Soc. Rev.* **2010**, *39*, 540–548; j) S.-l. You, J.-B. Xia, *Top. Curr. Chem.* **2010**, *292*, 165–194; k) T. C. Boorman, I. Larrosa, *Chem. Soc. Rev.* **2011**, *40*, 1910–1925; l) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, *Chem. Soc. Rev.* **2011**, *40*, 5068–5083; m) J. Le Bras, J. Muzart, *Chem. Rev.* **2011**, *111*, 1170–1214; n) C. Liu, H. Zhang, W. Shi, A. Lei, *Chem. Rev.* **2011**, *111*, 1780–1824; o) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215–1292; p) A. N. Campbell, S. S. Stahl, *Acc. Chem. Res.* **2012**, *45*, 851–863.

[5] a) B. Yang, T.-T. Yang, X.-A. Li, J.-J. Wang, S.-D. Yang, *Org. Lett.* **2013**, *15*, 5024–5027; b) Y.-M. Li, M. Sun, H.-L. Wang, Q.-P. Tian, S.-D. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3972–3976; *Angew. Chem.* **2013**, *125*, 4064–4068; c) Y.-R. Chen, W.-L. Duan, *J. Am. Chem. Soc.* **2013**, *135*, 16754–16757; d) X.-Q. Pan, L. Wang, J.-P. Zou, W. Zhang, *Chem. Commun.* **2011**, *47*, 7875–7877; e) Y. Gao, G. Wang, L. Chen, P. Xu, Y. Zhao, Y. Zhou, L.-B. Han, *J. Am. Chem. Soc.* **2009**, *131*, 7956–7957; f) S. H. Kim, K. H. Kim, J. W. Lim, J. N. Kim, *Tetrahedron Lett.* **2014**, *55*, 531–534; g) C. Li, T. Yano, N. Ishida, M. Murakami, *Angew. Chem. Int. Ed.* **2013**, *52*, 9801–9804; *Angew. Chem.* **2013**, *125*, 9983–9986; h) C. Hou, Y. Ren, R. Lang, X. Hu, C. Xia, F. Li, *Chem. Commun.* **2012**, *48*, 5181–5183; i) C.-G. Feng, M. Ye, K.-J. Xiao, S. Li, J.-Q. Yu, *J. Am. Chem. Soc.* **2013**, *135*, 9322–9325.

[6] a) O. Baslé, C.-J. Li, *Chem. Commun.* **2009**, 4124–4126; b) W. Han, A. R. Ofial, *Chem. Commun.* **2009**, 6023–6025; c) M. Rueping, S. Zhu, R. M. Koenigs, *Chem. Commun.* **2011**, *47*, 8679–8681; d) D. Das, D. Seidel, *Org. Lett.* **2013**, *15*, 4358–4361; e) W.-J. Yoo, S. Kobayashi, *Green Chem.* **2014**, *16*, 2438–2442.

[7] a) D. Uraguchi, T. Ito, S. Nakamura, T. Ooi, *Chem. Sci.* **2010**, *1*, 488–490; b) J. Zheng, X. Feng, Y. Yu, X. Zhen, Y. Zhao, *Phosphorus Sulfur Silicon Relat. Elem.* **2013**, *188*, 1080–1087.

[8] a) U. Jahn, *Top. Curr. Chem.* **2012**, *320*, 191–322; b) U. Jahn, *Top. Curr. Chem.* **2012**, *320*, 323–452; c) X.-Q. Hu, J.-R. Chen, Q. Wei, F.-L. Liu, Q.-H. Deng, A. M. Beauchemin, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2014**, *53*, 12163–12167; *Angew. Chem.* **2014**, *126*, 12359–12363; d) M. Grzybowski, K. Skonieczny, H. Butenschoen, D. T. Gryko, *Angew. Chem. Int. Ed.* **2013**, *52*, 9900–9930; *Angew. Chem.* **2013**, *125*, 10084–10115; e) J. J. Mousseau, A. B. Charette, *Acc. Chem. Res.* **2013**, *46*, 412–424; f) S. Zhu, A. Das, L. Bui, H. Zhou, D. P. Curran, M. Rueping, *J. Am. Chem. Soc.* **2013**, *135*, 1823–1829; g) Z. Shi, C. Zhang, C. Tang, N. Jiao, *Chem. Soc. Rev.* **2012**, *41*, 3381–3430; h) C. Zhang, C. Tang, N. Jiao, *Chem. Soc. Rev.* **2012**, *41*, 3464–3484.

[9] D. Leca, L. Fensterbank, E. Lacote, M. Malacria, *Chem. Soc. Rev.* **2005**, *34*, 858–865.

[10] a) A. Bravo, H.-R. Bjorsvik, F. Fontana, L. Liguori, F. Minisci, *J. Org. Chem.* **1997**, *62*, 3849–3857; b) K.-S. Focsaneanu, C. Aliaga, J. C. Scaiano, *Org. Lett.* **2005**, *7*, 4979–4982; c) R. Spaccini, N. Pastori, A. Clerici, C. Punta, O. Porta, *J. Am. Chem. Soc.* **2008**, *130*, 18018–18024; d) W. Liu, Y. Li, K. Liu, Z. Li, *J. Am. Chem. Soc.* **2011**, *133*, 10756–10759; e) B. Schweitzer-Chaput, J. Demaerel, H. Engler, M. Klussmann, *Angew. Chem. Int. Ed.* **2014**, *53*, 8737–8740; *Angew. Chem.* **2014**, *126*, 8882–8885; f) C. Liu, D. Liu, A. Lei, *Acc. Chem. Res.* **2014**, *47*, 3459–3470; g) L. Zhou, S. Tang, X. Qi, C. Lin, K. Liu, C. Liu, Y. Lan, A. Lei, *Org. Lett.* **2014**, *16*, 3404–3407; h) J. Xuan, T.-T. Zeng, Z.-J. Feng, Q.-H. Deng, J.-R. Chen, L.-Q. Lu, W.-J. Xiao, H. Alper, *Angew. Chem. Int. Ed.* **2015**, *54*, 1625–1628; *Angew. Chem.* **2015**, *127*, 1645–1648.

[11] a) D. Griller, K. U. Ingold, *Acc. Chem. Res.* **1976**, *9*, 13–19; b) H. Fischer, *Chem. Rev.* **2001**, *101*, 3581–3610.

[12] P.-C. Too, Y.-F. Wang, S. Chiba, *Org. Lett.* **2010**, *12*, 5688–5691.

[13] a) Z.-H. Ren, Z.-Y. Zhang, B.-Q. Yang, Y.-Y. Wang, Z.-H. Guan, *Org. Lett.* **2011**, *13*, 5394–5397; b) P. C. Too, S. H. Chua, S. H. Wong, S. Chiba, *J. Org. Chem.* **2011**, *76*, 6159–6168; c) H. Huang, X. Ji, X. Tang, M. Zhang, X. Li, H. Jiang, *Org. Lett.* **2013**, *15*, 6254–6257; d) X. Tang, L. Huang, C. Qi, W. Wu, H. Jiang, *Chem. Commun.* **2013**, *49*, 9597–9599; e) Y. Wei, N. Yoshikai, *J. Am. Chem. Soc.* **2013**, *135*, 3756–3759; f) X. Tang, L. Huang, Y. Xu, J. Yang, W. Wu, H. Jiang, *Angew. Chem. Int. Ed.* **2014**, *53*, 4205–4208; *Angew. Chem.* **2014**, *126*, 4289–4292; g) Z.-J. Cai, X.-M. Lu, S.-Y. Wang, S.-J. Ji, *Acta Chim. Sin.* **2014**, *72*, 914–919.

[14] a) K. K. Toh, Y.-F. Wang, E. P. J. Ng, S. Chiba, *J. Am. Chem. Soc.* **2011**, *133*, 13942–13945; b) K. K. Toh, A. Biswas, Y.-F. Wang, Y. Y. Tan, S. Chiba, *J. Am. Chem. Soc.* **2014**, *136*, 6011–6020.

[15] Y. Sueishi, Y. Nishihara, *Chem. Res. Chin. Univ.* **2000**, *16*, 313–319.

Received: February 9, 2015