Letter

Visible Light-induced External Oxidant-free Oxidative Phosphonylation of C(sp2)-H Bonds

Linbin Niu, Jiamei Liu, Hong Yi, Shengchun Wang, Xing-An Liang, Atul Kumar Singh, Chien-Wei Chiang, and Aiwen Lei

ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.7b02418 • Publication Date (Web): 27 Sep 2017

Visible Light-Induced External Oxidant-Free Oxidative Phosphonylation of C(sp²)-H Bonds

Linbin Niu,[1] Jiamei Liu,[1] Hong Yi,[1] Shengchun Wang,[1] Xing-An Liang,[1] Atul Kumar Singh,[1] Chien-Wei Chiang,[1] and Aiwen Lei[1,2]*

1. College of Chemistry and Molecular Sciences, Institute for Advanced Studies (IAS), Wuhan University, Wuhan, Hubei 430072, P. R. China.

2. State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China.

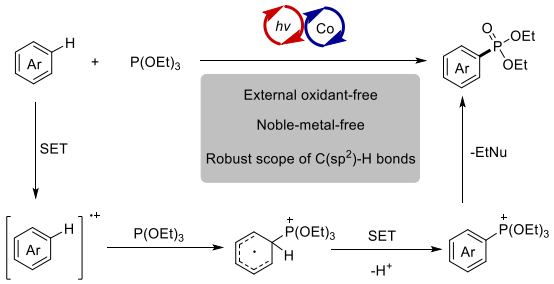
ABSTRACT: Considering the synthetic value of phosphonates, developing powerful catalytic methods for the phosphonylation of C(sp²)-H bonds is important. Herein, we achieve a visible light-induced external oxidant-free oxidative phosphonylation of C(sp²)-H bonds via the combination of photocatalysis and proton-reduction catalysis. Mechanistic studies indicate visible light-induced electron-rich arene radical cation is the key reactive intermediate. The synthetic application of this approach is demonstrated in the late-stage functionalization of pharmaceutical molecules. This study may have significant implications for the functionalization of C(sp²)-H bonds, especially for those which are sensitive to oxidative conditions.

KEYWORDS: Photocatalysis, External oxidant-free, Proton-reduction catalysis, Phosphonylation, C(sp²)-H bonds, Radical cation

Due to aryl and vinyl phosphonates being incorporated into a vast number of structural diverse molecules which involve in organic synthesis, agrochemical, material chemistry, and biochemistry,[1] mild and sustainable catalytic phosphonylation strategies are considered highly desirable. The pioneering work of constructing C(sp²)-P bonds by palladium-catalyzed cross coupling of an aryl halide with H-phosphonate was reported by Hirao et al.[2] Since then, transition-metal-catalyzed phosphonylation of various C(sp²)-X has been served as a general route to forge C(sp²)-P bonds.[3] In spite of possessing regiospecificity, the key limitation of the method is in need of pre-functionalized starting material. There is no doubt that oxidative phosphonylation of C(sp²)-H bonds is the most direct method for C(sp²)-P bonds construction.

Various strategies for oxidative phosphonylation of C(sp²)-H bonds have been developed in recent years. Transition-metal-catalyzed and chemical oxidants dominating the oxidative C(sp²)-H bonds phosphonylation are regarded as important synthetic advances.[4] However, these transformations regularly require directing groups, stoichiometric oxidants or inevitably rigorous reaction temperature. Recently, photochemistry has been an attractive way to realize some challenging chemistry conversions.[5] Particularly, visible light-induced oxidative phosphonylation of C(sp²)-H bonds by photo/oxidant catalytic system has provided an efficient access to C(sp²)-P bonds.[6] Even so, the introduction of stoichiometric quantities of oxidants as dehydrogenation agent and electron acceptor limits its application, especially causing the circumscribed functional group compatibility and oxidative side reactions.[6b] Having recognized the importance of aryl and vinyl phosphonates, and the limitation of previous reports about oxidative phosphonylation of C(sp²)-H bonds, we hope to develope a noble metal-free, external oxidant-free and harsh temperature-free oxidative phosphonylation method for C(sp²)-H bonds. Inspired by the photoinduced oxidative cross-coupling between two nucleophiles under the oxidant-free condition,[7] herein, we demonstrate an external oxidant-free oxidative phosphonylation of C(sp²)-H bonds (methylarenes, anisoles, polycyclic aromatic hydrocarbons, heteroaromatics, anilines and olefins derivatives) with no need for excess phosphonylation reagents by merging visible-light photoredox with cobalt catalysis. By adopting this strategy, the late-stage functionalization of the pharmaceutical molecules can be successfully carried out.

Scheme 1. The oxidative phosphonylation of C(sp²)-H bonds under visible light-induced external oxidant-free conditions.

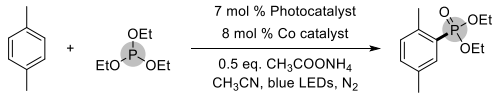


Our strategy for phosphonylation of C(sp²)-H bonds is based on the capture of the crucial arenes and olefins radical cations (Scheme 1). Simple arenes and olefins can undergo a single electron transfer (SET) step with some excited photocatalysts whose oxidative ability are strong under light irradiation.[7] The generated radical cation species can be trapped by phosphites, and followed by another SET step and the subsequent deprotonation step, delivering the cation intermediate. Finally, the nucleophilic displacement step gives the final captured product.[4b]

To this end, after optimization, a satisfactory yield 92% (**3a**) of the oxidative C(sp²)-H phosphonylation was reaped with the *p*-xylene (**1a**) and triethyl phosphite (**2a**) by merging photoredox and cobalt catalysis, whereas the benzyl group was unaffected (Table 1, entry 3). To unambiguously develop this

phosphonylativon protocol (Table S1),[8] the investigation of photocatalyst was carried out primarily. As we can see, the failure that no phosphonylation product was obtained when $Ru(bpy)_3(PF_6)_2$ and Eosin Y were employed as the photocatalyst (Table 1, entries 1 and 2), contrastively revealed that an adequately high oxidizing capability of the excited photocatalyst to induce a SET step is the crucial requirement. Due to the volatility of the arene,[9, 7d] the yield for the phosphonylation product dropped to 61% when the concentration of arene was lowered to one stoichiometric level (Table 1, entry 4). In absence of photocatalyst, cobalt catalyst or light, the reaction couldn't be promoted, indicating that all the components are essential for this visible light-induced external oxidant-free phosphonylation protocol (Table 1, entries 5, 6 and 7). Meanwhile, ammonium acetate was necessary which might act as a nucleophile to facilitate the nucleophilic displacement (Table 1, entry 8).[4b] It was noteworthy that phosphonylation of $C(sp^2)$-H bonds showed extremely poor reactivity due to the overoxidation of methylarenes and phosphites, when the reaction was mediated by O_2 or stoichiometric oxidants such as sodium persulfate ($Na_2S_2O_8$) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Table 1, entries 9, 10 and 11, see Supporting Information for details, Table S2). In comparison to photo/oxidant catalytic system, this visible light-induced external oxidant-free oxidative phosphonylation protocol overcomes the limitation of overoxidation and provides an ideal alternative for the synthesis of aryl phosphonates.

Table 1. Investigation of the reaction conditions.[a]



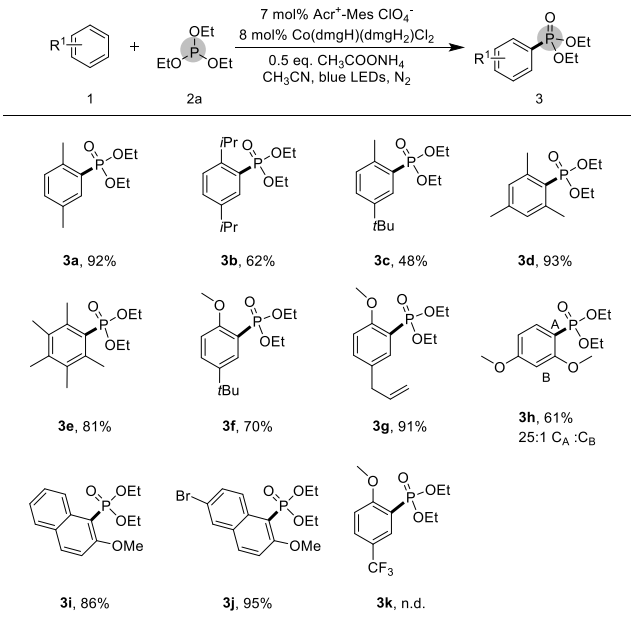
1a **2a** **3a**

Entry	Photocatalyst	Co catalyst	Yield (%)[b]
1	$Ru(bpy)_3(PF_6)_2$	$Co(dmgH)(dmgH_2)Cl_2$	n.d.
2	Eosin Y	$Co(dmgH)(dmgH_2)Cl_2$	n.d.
3	Acr^+-Mes ClO_4^-	$Co(dmgH)(dmgH_2)Cl_2$	92 (92)[c]
4[d]	Acr^+-Mes ClO_4^-	$Co(dmgH)(dmgH_2)Cl_2$	61
5	-	$Co(dmgH)(dmgH_2)Cl_2$	n.d.
6	Acr^+-Mes ClO_4^-	-	n.d.
7[e]	Acr^+-Mes ClO_4^-	$Co(dmgH)(dmgH_2)Cl_2$	n.d.
8[f]	Acr^+-Mes ClO_4^-	$Co(dmgH)(dmgH_2)Cl_2$	trace
9	Acr^+-Mes ClO_4^-	O_2 instead	14
10	Acr^+-Mes ClO_4^-	$Na_2S_2O_8$ instead	15
11	Acr^+-Mes ClO_4^-	DDQ instead	10

[a]Conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), photocatalyst (7 mol%), Co catalyst (8 mol%), 0.5 eq. CH_3COONH_4 in 3.0 mL CH_3CN under a nitrogen atmosphere, irradiated by 3 W blue LEDs, r.t., 24 h; [b]GC yields with naphthalene as the internal standard; [c]isolated yield within parentheses; [d]1.0 equiv. arene was used; [e]without light; [f]without CH_3COONH_4.

With the suitable condition in hand, all kinds of $C(sp^2)$-H bonds were extended to the phosphonylation protocol. In consideration of methylarenes as versatile building blocks in organic synthesis,[10] various alkyl-substituted benzenes were firstly investigated. As shown in Scheme 2, what's particularly noteworthy was the perfect chemoselectivity that only $C(sp^2)$-H phosphonylation occurred regardless of the existence of the sensitive benzyl $C(sp^3)$–H bond, when benzene ring bears isopropyl substituent (**3b**). What's more, 1-(*tert*-butyl)-4-methylbenzene delivered the targeted aryl phosphonates product in single site-selectivity (**3c**). In spite of the bulky steric hindrance that the polyalkyl-substituted benzenes possess, the reaction was still processed with high efficiency (**3d** and **3e**). Likewise, anisole derivatives with different functional groups were probed to show good functional group tolerance. It was notable that 1-(*tert*-butyl)-4-methoxybenzene behaved a good yield with excellent selectivity (**3f**). Notably, the phosphonylation of 1-allyl-4-methoxybenzene was carried out with sole chemoselectivity and site-selectivity (**3g**). We were delighted that meta-substituted anisole was phosphonylated in satisfying regioselectivity (**3h**). Importantly, π-extended aryl ether and derivatives could be well tolerable and provide an opportunity for the modification of some drug molecules which contain naphthalene skeleton (**3i** and **3j**). We then chose 2-methoxynaphthalene (**1i**) to scale up this phosphonylation protocol, which was smoothly amenable to gram-scale synthesis in a good yield 83%, providing a promising synthetic route for phosphonylation of $C(sp^2)$-H bonds (Figure S3). Unfortunately, there was no reactivity for 4-(trifluoromethyl)anisole due to the difficulty of being oxidized by excited photocatalyst (**3k**).

Scheme 2. Substrate scope for the oxidant-free phosphonylation of methylarenes and anisoles with $P(OEt)_3$.[a]

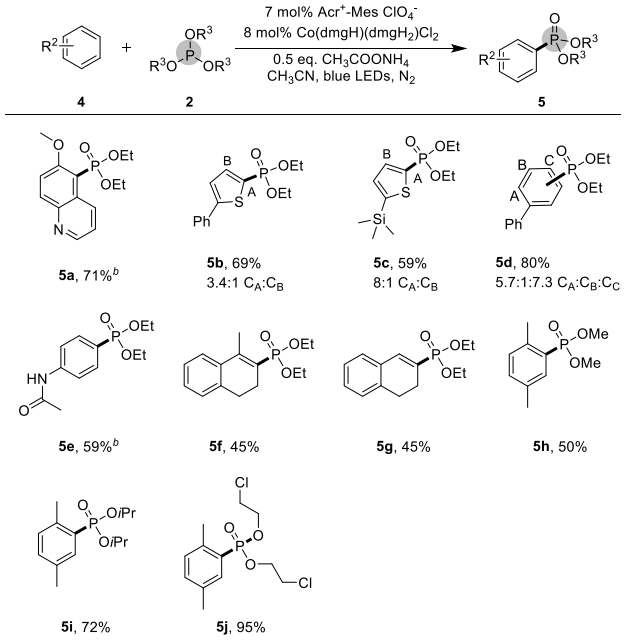


[a]Conditions: **1** (0.4 mmol), **2a** (0.2 mmol), Acr^+-Mes ClO_4^- (7 mol%), $Co(dmgH)(dmgH_2)Cl_2$ (8 mol%), 0.5 eq. CH_3COONH_4 in 3.0 mL CH_3CN under a nitrogen atmosphere, irradiated by 3 W blue LEDs, r.t., 24 h; isolated yields. The ratio of the isomers was determined by NMR.

The unprecedented reactivity encouraged us to explore the phosphonylation of more general and valuable $C(sp^2)$-H bonds

(Scheme 3). Indeed, the high-yield phosphonylation of heterocycles, olefins and anilines derivatives with good selectivity still remain rare. Notably, the procedure can be expanded to quinoline bearing electron-releasing substitution (**5a**). Electron-rich thiophene compounds such as 2-phenylthiophene and trimethyl(thiophen-2-yl)silane were successfully phosphonylated in satisfactory yield and modest selectivity (**5b** and **5c**). It was disappointed that the phosphonylation of indoles failed under the standard condition. Biphenyl displayed a good reaction activity but the inseparable isomers were obtained (**5d**). Even acetyl-protected aniline was still a competent substrate, because the single selectivity seemed to be effortlessly obtained (**5e**). Significantly, the phosphonylation product serves as a key intermediate to access to GPAT inhibitor.[11] It is important that olefins were also suitable for this system and achieved the desired products with the sole chemoselectivity (**5f** and **5g**), which further demonstrated the universality of this novel and powerful phosphonylation method. Unfortunately, the not-styrene-based olefin like cyclohexene couldn't be phosphonylated due to the high oxidation potential ($E_{1/2\ ox}$ = +2.37 V vs SCE).[12] Additionally, we also made our attempts to use other different phosphites to achieve the phosphonylation of C(sp^2)-H bonds under this catalytic system. For trialkyl phosphites, $P(OMe)_3$ provided a modest yield (**5h**) and $P(OiPr)_3$ was a satisfactory phosphonylation reagent despite of the possible steric bulk (**5i**). Moreover, excellent reactivity was demonstrated when tris(2-chloroethyl) phosphite was applied (**5j**).

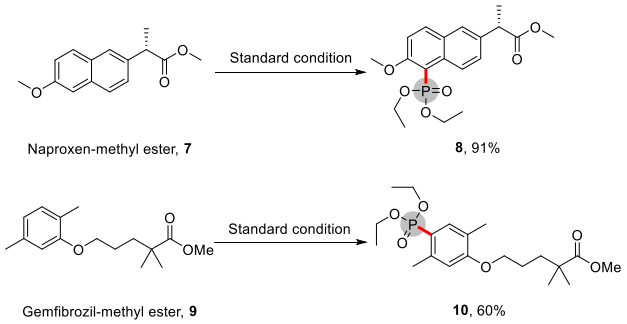
Scheme 3. Substrate scope for the oxidant-free phosphonylation of other extended C(sp^2)-H bonds.[a]



[a]Conditions: **4** (0.4 mmol), **2** (0.2 mmol), Acr^+-Mes ClO_4^- (7 mol%), Co(dmgH)($dmgH_2$)Cl_2 (8 mol%), 0.5 eq. CH_3COONH_4 in 3.0 mL CH_3CN under a nitrogen atmosphere, irradiated by 3W blue LEDs, r.t., 24 h; isolated yields. [b]4.0 mL of CH_3CN was used. The ratio of the isomers was determined by NMR.

Additionally, the late-stage functionalization of several drug-like molecules (**7** and **9**) were designed to highlight the synthetic value of our catalytic strategy (Scheme 4). Not only the good efficiency but also the aim of site-selective phosphonylation were successfully achieved (**8** and **10**). Simultaneously, the highly reactive benzyl C(sp^3)-H bonds were preserved. The pioneering result is expected to bring about the late-stage phosphonylation of more complex and meaningful molecules.

Scheme 4. Late-stage functionalization of drug-like molecules.



The detailed mechanistic studies was demonstrated to reveal some important hints of this visible light-induced external oxidant-free phosphonylation protocol. In the presence of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, 2 equiv.) or 2,6-di-*tert*-butyl-4-methylphenol (BHT, 2 equiv.), the inhibition of the reaction efficiency indicated that a radical process might be involved (Figure S4).

Thereafter, we designed the intermolecular kinetic isotope effect experiment, which afforded the KIE value in 1.25 (Figure 1), revealing that the rate-determining step might not take place in the cleavage of C(sp^2)-H (see Supporting Information for details, Figure S5 and S6). Simultaneously, no O^{18} labeling aryl phosphonate was detected in H_2O^{18} labeling experiment, which excluded the participation of water in the reaction pathway (Figure S7).

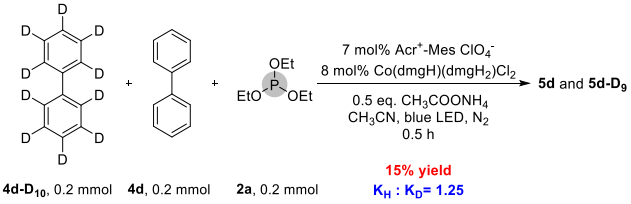


Figure 1. The intermolecular kinetic of isotopic effect experiment.

From the outset, we anticipated that the initial SET step is originated from the single electron oxidation of C(sp^2)-H bonds by excited photocatalyst. With the aim of gaining convincing evidence, a series of photoluminescence quenching experiments were designed (see Supporting Information for details , Figure S8). The photoluminescence of the photocatalyst Acr^+-Mes ClO_4^- was obviously quenched by methylarenes, anisoles, anilines and olefins derivatives. In contrast, nearly no quenching was behaved when $P(OEt)_3$ **2a** was employed as a quencher. Moreover, $P(OPh)_3$ **2k** decomposed into phenol **6** under this reaction condition, failing to produce any corresponding phosphonylated products **5k** (Figure S11). This is why the arene and olefin radical cations were considered as the critical reaction intermediates.

Based on the experimental results of mechanistic investigation, we presumed that the arene or olefin radical cations are pivotal intermediates for the phosphonylation of

C(sp^2)-H bonds. Taking *p*-xylene **1a** as an example, a plausible mechanistic cycle for this C(sp^2)-H phosphonylation was outlined in Figure 2. Initially, the excited state acridinium photocatalyst[13] excited by the irradiation of commercial available blue LEDs is capable of oxidizing *p*-xylene **1a**, generating the Acr^+-Mes ClO_4^- radical and the corresponding arene radical cation **11**. Herein, we believe that the $P(OEt)_3$ **2a** acts as a nucleophile to capture the arene radical cation, and delivers the adduct **12**. Then, the proton-reduction Co(III) catalyst is responsible for producing the intermediate **13** by a single electron transfer, which oneself be reduced to give the Co(II). A rapid deprotonation affords the phosphorus cation intermediate **14**. With the help of the additive CH_3COONH_4 leading a nucleophilic displacement step,[4b] the aryl phosphonium salt **14** is converted into the final phosphonylation product **3a**.[14] It is considered that the regeneration of the photocatalyst is resulted from the oxidation by Co(II) and generates Co(I). As a result, the protonation of Co(I) affords Co(III)-H[15] and H_2 can be released by the protonation of Co(III)-H to accomplish the Co catalytic cycle.

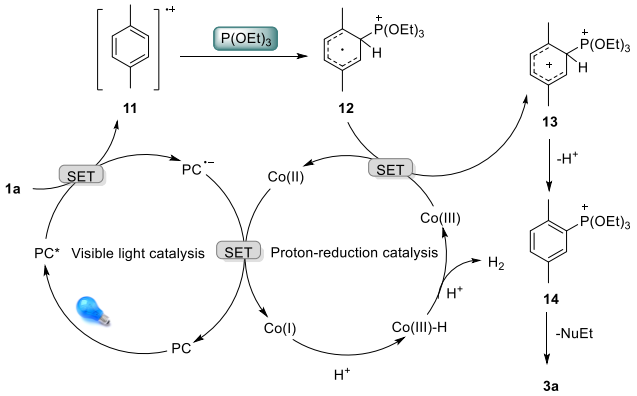


Figure 2. Proposed mechanism for visible light-induced oxidant-free oxidative C(sp^2)-H phosphonylation (PC: photocatalyst Acr^+-Mes ClO_4^-; Co: Co(dmgH)(dmgH$_2$)Cl$_2$ catalyst).

In conclusion, we have demonstrated a mild and chemoselective nature of visible light-induced external oxidant-free oxidative phosphonylation of C(sp^2)-H bonds. Various kinds of C(sp^2)-H bonds including methylarenes, anisoles, polycyclic aromatic hydrocarbons, heteroaromatics, anilines and olefins derivatives can be phosphonylated efficiently, making it appealing for late stages of synthesis programs. Moreover, mechanistic studies show that the single electron oxidation of electron-rich aromatic rings or olefins is the key reaction step for this phosphonylation conversion. The development of related functionalization of C(sp^2)-H bonds is underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information.
The Supporting Information is available free of charge via the Internet at http://pubs.acs.org, which included NMR data; extended data about mechanism study, condition investigation, and characterization (PDF)

AUTHOR INFORMATION

Corresponding Author

* Corresponding author, E-mail: aiwenlei@whu.edu.cn.

Notes

The authors declare no competing financial interest.

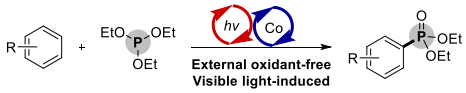
ACKNOWLEDGMENT

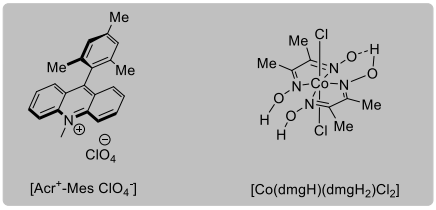
This work was supported by the 973 Program (2011CB808600, 2012CB725302, 2013CB834804), the National Natural Science Foundation of China (21390400, 21272180, 21302148, 2109343 and 21402217), and the Research Fund for the Doctoral Program of Higher Education of China (20120141130002) and the Ministry of Science and Technology of China (2012YQ120060) and the Program for Changjiang Scholars and Innovative Research Team in University (IRT1030). The Program of Introducing Talents of Discipline to Universities of China (111 Program) is also appreciated.

REFERENCES

(1) (a) Moonen, K.; Laureyn, I.; Stevens, C. V. *Chem. Rev*. **2004**, *104*, 6177-6216; (b) Branion, S.; Benin, V. *Synth. Commun*. **2006**, *36*, 2121-2127; (c) Guga, P. *Curr. Top. Med. Chem*. **2007**, *7*, 695-713; (d) Horsman, G. P.; Zechel, D. L. *Chem. Rev.* **2017**, *117*, 5704–5783.
(2) (a) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *Tetrahedron Lett*. **1980**, *21*, 3595-3598; (b) Hirao, T.; Masunaga, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn*. **1982**, *55*, 909-913.
(3) (a) Baillie, C.; Xiao, J. *Curr. Org. Chem.* **2003**, *7*, 477-514; (b) Demmer, C. S.; Krogsgaard-Larsen, N.; Bunch, L. *Chem. Rev.* **2011**, *111*, 7981-8006; (c) Gelman, D.; Jiang, L.; Buchwald, S. L. *Org. Lett*. **2003**, *5*, 2315-2318; (d) Zhuang, R.; Xu, J.; Cai, Z.; Tang, G.; Fang, M.; Zhao, Y. *Org. Lett*. **2011**, *13*, 2110-2113; (e) Zhao, Y.-L.; Li, Y.; Li, S.-M.; Zhou, Y.-G.; Sun, F.-Y.; Gao, L.-X.; Han, F.-S. *Adv. Synth. Catal*. **2011**, *353*, 1543–1550; (f) Zhang, H. Y.; Sun, M.; Ma, Y. N.; Tian, Q. P.; Yang, S. D. *Org. Biomol. Chem.* **2012**, *10*, 9627-9623.
(4) (a) Minisci, F.; Citterio, A.; Giordano, C. *Acc. Chem. Res*. **1983**, *16*, 27–32; (b) Effenberger, F.; Kottmann, H. *Tetrahedron* **1985**, *41*, 4171-4182; (c) Kottmann, H.; Skarzewski, J.; Effenberger, F. *Synthesis* **1987**, *9*, 797-801; (d) Kagayama, T.; Nakano, A.; Sakaguchi, S.; Ishii, Y. *Org. Lett*. **2006**, *8*, 407-409; (e) Feng, C. G.; Ye, M.; Xiao, K. J.; Li, S.; Yu, J. Q. *J. Am. Chem. Soc*. **2013**, *135*, 9322-9325; (f) Li, C.; Yano, T.; Ishida, N.; Murakami, M. *Angew. Chem., Int. Ed*. **2013**, *52*, 9801-9804; (g) Wang, S.; Guo, R.; Wang, G.; Chen, S. Y.; Yu, X. Q. *Chem. Commun*. **2014**, *50*, 12718-12721; (h) Chen, Z.; Wang, B.; Zhang, J.; Yu, W.; Liu, Z.; Zhang, Y. *Org. Chem. Front*. **2015**, *2*, 1107-1295; (i) Lin, W.; Su, F.; Zhang, H. J.; Wen, T. B. *Eur. J. Org. Chem*. **2017**, *13*, 1757-1759; (j) Wang, C.-S.; Dixneuf, P. H.; Soule, J.-F. *ChemCatChem.* **2017**, 10.1002/cctc.201700557.
(5) (a) Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, *2*, 527-532; (b) Narayanam, J. M.; Stephenson, C. R. *Chem. Soc. Rev.* **2011**, *40*, 102-113; (c) Xuan, J.; Xiao, W. J. *Angew. Chem., Int. Ed*. **2012**, *51*, 6828-6838; (d) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. *Chem. Rev*. **2013**, *113*, 5322-5363; (e) Hari, D. P.; Konig, B. *Angew. Chem., Int. Ed*. **2013**, *52*, 4734-4743; (f) Ravelli, D.; Protti, S.; Fagnoni, M. *Chem. Rev*. **2016**, *116*, 9850-9913; (g) Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, *116*, 10075-10166; (h) Ohkubo, K.; Fujimoto, A.; Fukuzumi, S. *J. Am. Chem. Soc*. **2013**, *135*, 5368-5371; (i) Romero, N. A.; Margrey, K. A.; Tay, N. E.; Nicewicz, D. A. *Science* **2015**, *349*, 1326-1330; (j) Hu, X. Q.; Qi, X.; Chen, J. R.; Zhao, Q. Q.; Wei, Q.; Lan, Y.; Xiao, W. J. *Nat. Commun.* **2016**, *7*, 11188-11200; (k) Quint, V.; Morlet-Savary, F.; Lohier, J. F.; Lalevée, J.; Gaumont, A. C.; Lakhdar, S. *J. Am. Chem. Soc.* **2016**, *138*, 7436-7441; (l) Bian, C.; Singh, A. K.; Niu, L.; Yi, H.; Lei, A. *Asian J. Org. Chem*. **2017**, *6*, 386-396; (m) Shaikh, R. S.; Düsel, S. J.; König, B. *ACS Catal*. **2017**, *6*, 8410-8414.
(6) (a) Zhao, Z.; Min, Z.; Dong, W.; Peng, Z.; An, D. *Synth. Commun*. **2016**, 46, 128-133; (b) Peng, P.; Peng, L.; Wang, G.; Wang, F.; Luo, Y.; Lei, A. *Org. Chem. Front*. **2016**, *3*, 749-752; (c) Shaikh, R.; Ghosh, I.; König, B. *Chem. - Eur. J.* **2017**, 10.1002/chem.201701283.
(7) (a) Zheng, Y. W.; Chen, B.; Ye, P.; Feng, K.; Wang, W.; Meng, Q. Y.; Wu, L. Z.; Tung, C. H. *J. Am. Chem. Soc*. **2016**, *138*, 10080-10083; (b) Zhang, G.; Hu, X.; Chiang, C.-W.; Yi, H.; Pei, P.; Singh, A. K.; Lei, A. *J. Am. Chem. Soc*. **2016**, *138*, 12037-12040; (c) Yi, H.; Niu, L.; Song,

C.; Li, Y.; Dou, B.; Singh, A. K.; Lei, A. *Angew. Chem., Int. Ed*. **2017**, *56*, 1120-1124; (d) Niu, L.; Yi, H.; Wang, S.; Liu, T.; Liu, J.; Lei, A. *Nat. Commun.* **2017**, *8*, 14226-14233.
(8) The conversion yields of the condition investigation were provided in the SI. In addition, the excess of arenes were recovered, and related byproducts weren't observed under this oxidant-free condition.
(9) Kantak, A. A.; Potavathri, S.; Barham, R. A.; Romano, K. M.; DeBoef, B. *J. Am. Chem. Soc.* **2011**, *133*, 19960–19965.
(10) Vanjari, R.; Singh, K. N. *Chem. Soc. Rev.* **2015**, *44*, 8062-8096.
(11) Wydysh, E. A.; Medghalchi, S. M.; Vadlamudi, A.; Townsend, C. A. *J. Med. Chem*. **2009**, *52*, 3317-3327.
(12) Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, *27*, 714–723.
(13) Romero, N. A.; Nicewicz, D. A. *J. Am. Chem. Soc*. **2014**, *136*, 17024-17035.
(14) The further phosphonylation of products weren't detected by LC-MS because the electron-rich arenes are excess and the phosphite esters are limited. Moreover, the cyclic voltammetry experiments of representative products were shown in SI.
(15) (a) Artero, V.; Chavarot-Kerlidou, M.; Fontecave, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 7238-7266; (b) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B. *Acc. Chem. Res.* **2009**, *42*, 1995-2004.


R
EtO
OEt
P
OEt
hv
Co
External oxidant-free
Visible light-induced
R
O
P
OEt
OEt


Me
Me
Me
N
ClO4
[Acr+-Mes ClO4-]
Me
Cl
Me
N
O
H
O
N
Co
N
O
H
O
N
Me
Me
Cl
[Co(dmgH)(dmgH2)Cl2]