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COMMUNICATION

New Oxime Phosphonates Participated Visible Photocatalysis: Synthesis of *β*-Aminophosphonates

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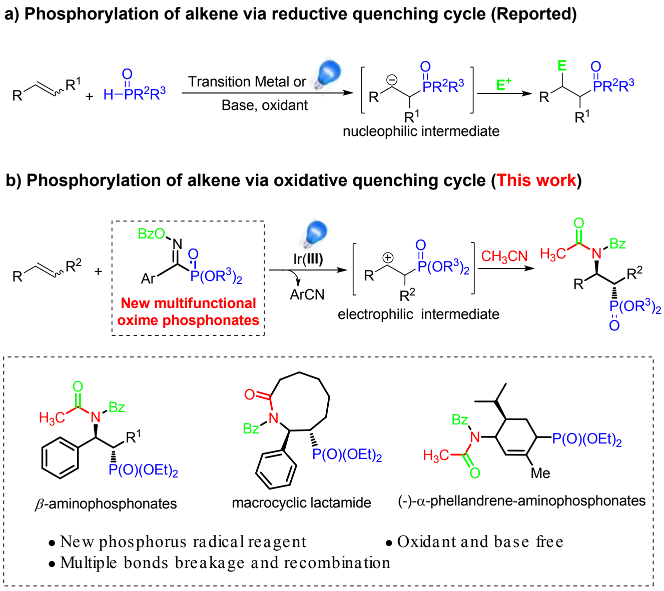
A new type of oxime phosphonates was firstly synthesized and used in the intermolecular cascade radical addition reaction of alkenes to access *β*-aminophosphonates via visible-light-driven *N*-centered iminyl radical-mediated and redox-neutral selective C–P single-bond cleavage in an active phosphorus radical route. The procedure is characterized by its ability to achieve the construction of Csp^3–P and Csp^3–N bonds without the requirement for oxidants and bases.

Difunctionalization of alkenes[1] using phosphorus-centered radicals has become a powerful strategy for the preparation of various *β*-functionalized phosphonates.[2] Advantages of this strategy include high efficiency and step economy. However, existing some deficiencies for the preparation of phosphorus radicals still remain to be settled; e.g., it is often necessary to add stoichiometric amounts of oxidants, bases, or various additives to the reaction system, which result in the generation of copious stoichiometric waste. Furthermore, the addition of equivalent oxidants not only impairs the scope of substrate and evokes the issue of chemoselectivity, it also generates obnoxious byproducts. In efforts to establish cleaner and more environmentally friendly reactions, new strategies and reagents for the phosphorus-centered radical difunctionalization of alkene without the requirement for external oxidants, bases, or various additives, are desirable. Very recently, the use of visible light photoredox catalysis[3] to generate phosphorus radical has been reported because this tactics offers more sustainable chemical processes. The reaction conditions are mild, thereby allowing for the potential ability to involve multiple catalytic pathways. However, in the vast majority of transition-metal-catalyzed or visible-light-driven phosphorus radical reactions, H-phosphonates have been used as substrates and added to alkene leading to form carbon nucleophilic intermediate (**a**, **Scheme 1**). In this transformation, the formation of the phosphorus radical still requires the assistance of an external bases or oxidants, which does not satisfy the requirement of the environmental friendliness or cleanliness of reactions.

It is known that Ir(III)-complex-prompted photoredox reactions involved in an oxidative quenching cycle,[4] which has rarely been applied to the phosphorus radical reactions for the H-phosphonates unsuitable for this photooxidation process. Thus, searching for a new oxidizing phosphorus radical reagent that produced not only a phosphorus radical, but also oxidized Ir(III)* to Ir(IV), subsequently forming a carbocation intermediate, then trapped by a nucleophile to achieve alkene difunctionalization is desirable and challenge. Based on these insights, we investigated and synthesized new phosphine sources of oxime-containing phosphonates.[5] The latter were



Scheme 1. Strategy for visible photocatalysis to construct *β*-aminophosphonates

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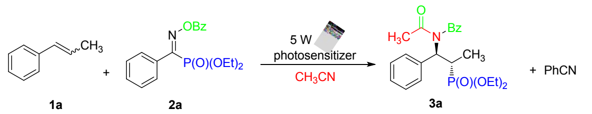
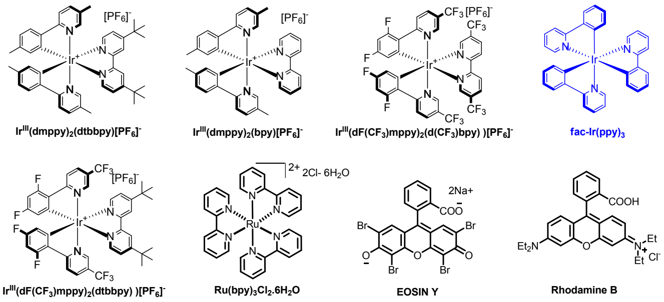
used for the intermolecular radical addition cascade reaction of alkenes to access *β*-functionalized phosphonates via visible-light-driven *N*-centered iminyl radical-mediated multiple bond cleavage and recombination process (**b**, **Scheme 1**). Use of this new phosphorus radical reagent not only avoids the requirement for the addition of external oxidants and bases, but also used in conjunction with photocatalysis to achieve more sustainable and environmentally friendly processes.

Oximes and their derivatives have relatively high oxidability. So, that it is relatively easy to prepare the highly reactive imine radical species by cleavage of the N–O bond under heating or illumination.[6] The iminyl radical is rapidly converted to form other more stable radicals through the release of an oxygen anion and intramolecular rearrangement.[7] Phosphoryl oxime ethers not only provide the phosphorus radical, but also as the oxidant to actualize Ir(III)* to Ir(IV) in the reaction simultaneously. Thus, we synthesized the diethyl [(benzoyloxy)imino](phenyl)methylphosphonate (**2a**), which was storability and stability toward moisture and oxygen,[5] and attempted to carry out the difunctionalization of alkenes through the visible-light-promoted oxidative quenching tactics under oxidant- and base-free conditions (**Table 1**). Various of photocatalysts were firstly screened with acetonitrile as solvent, the new difunctionalization of alkene really occured and the *β*-aminophosphonate of **3a** was obtained in 77% yield by using *fac*-Ir(ppy)$_3$ as catalyst. In this transformation, acetonitrile not only acted as solvent, but also as substrate participated in the reaction of involving the multiple bond cleavage and recombination process. Inspired by this result, We further optimized reaction conditions and results revealed that the loading of the photocatalyst *fac*-Ir(ppy)$_3$ could be reduced to 0.5 mol % with no change in the yield. Control experiments revealed that the *fac*-Ir(ppy)$_3$ and visible light irradiation are essential for the reaction.

Table 1. Screening of Reaction Conditions*^{a}*



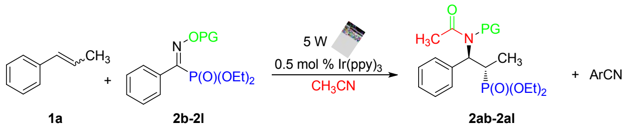
entry	photocatalyst (mol %)	result^b
1	Ir^{III}(dmppy)$_2$(dtbbpy)PF$_6$ (1)	N.R.
2	Ir^{III}(dmppy)$_2$(bpy)PF$_6$ (1)	N.R.
3	Ir^{III}(dF(CF$_3$)mppy)$_2$(dtbbpy)PF$_6$ (1)	N.R.
4	Ir^{III}(dF(CF$_3$)mppy)$_2$(d(CF$_3$)bpy)PF$_6$ (1)	N.R.
5	*fac*-Ir(ppy)$_3$ (1)	77%
6	*fac*-Ir(ppy)$_3$ (0.5)	77%
7		N.R.
8^c	*fac*-Ir(ppy)$_3$ (0.5)	N.R.
9	Ru(bpy)$_3$Cl$_2$·6H$_2$O (1)	N.R.
10	Eosin Y (5)	N.R.
11	Rhodamine B (5)	N.R.

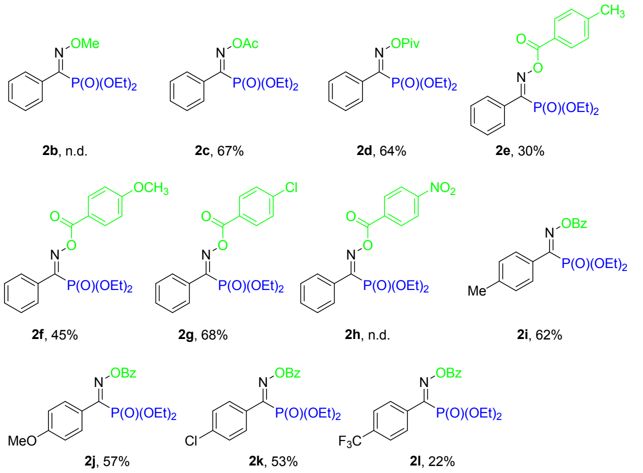


^{a}Reaction conditions: a solution of **1a** (1.5 equiv), **2a** (1.0 equiv), photocatalyst (1.0 mol %) in CH$_3$CN (0.25 M) was irradiated by 5W Blue LED lamp at rt for 8 h under Ar. ^{b}Isolated yield. ^{c}N.R.= No Reaction.

β-Aminophosphonates are isosteres of *β*-amino acid derivatives,[8] which are reported to possess various biological activities and potential medicinal properties,including antibacterial,[9] enzyme inhibitors,[10] catalytic antibio tics,[11] anti-HIV,[12] and anti-inflammatory[13] activities. In the next, we synthesized different phosphoryl oxime ethers and investigated their activities in this transformation (**Table 2**). When the protecting group on the oxygen atom is the methyl (**2b**) or 4-nitrobenzoyl (**2h**), the reaction did not proceed. However, when using different acyls such as -Ac, -Piv, -Bz, and 4-arylbenzoyl (instead of methyl group) as protecting groups, the reactions proceeded smoothly (**2c**–**2g**). Reactions of oximes with some other aryl groups (**2i**–**2l**) also proceed, albeit with lower yields.

Table 2. Screening of phosphine sources*^{a,b}*

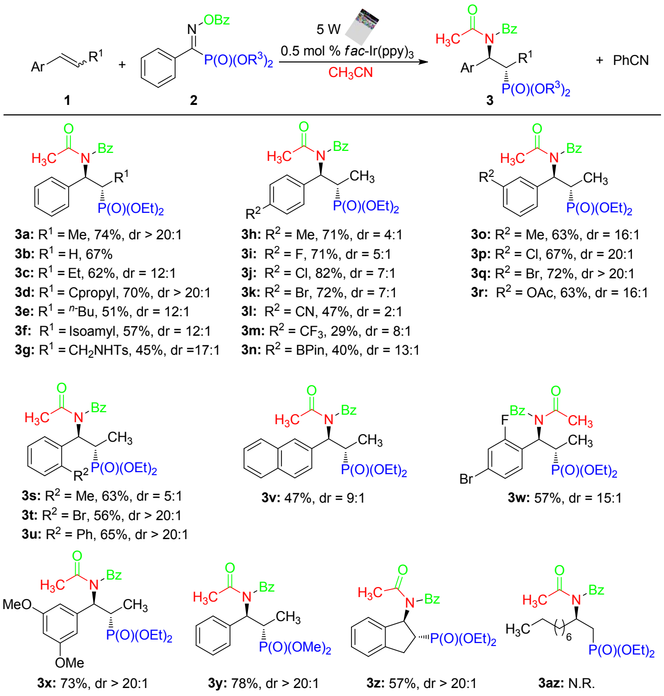




^{a}Reaction conditions: a solution of **1a** (1.5 equiv), **2** (1.0 equiv), photocatalyst (1.0 mol %) in CH$_3$CN (0.25 M) was irradiated by 5W Blue LED lamp at rt for 8 h under Ar. ^{b}Isolated yield.

With the optimal conditions in hand, a wide range of aromatic olefins were submitted to the photoredox catalysis protocol. First, we investigated the influence of the terminal group of styrene. As shown in **Table 3**, *β*-alkyl-substituted styrenes gave the corresponding products **3** in moderate to good yields (**3a**–**3h**). When the cpropyl group was introduced to the styrene, good yield and high diastereomeric ratio (dr) were obtained (**3d**, 70%, dr > 20:1). Next, we investigated a variety of substituted *β*-methyl styrene substrates (**3i**–**3u**, **3w**, **3x**). We were delighted that the reactions proceeded in moderate to good yields (29–82%) when electron-withdrawing and electron-donating groups were introduced into the para position of alkene. Furthermore, a wide range of *meta*- and *ortho*-substituted β-methyl styrenes were also tolerated in this transformation. Good yields were obtained (56–72%), particularly for **3q** and **3x**, both good yields and high dr were obtained (72%, dr > 20:1; 73%, dr > 20:1). When the naphthalene ring was used instead of benzene, a low yield was obtained (**3v**, 47%). When a methoxy group was used on the phosphorus instead of an oxyethyl group, good yield and dr value were obtained (78%, dr = 9:1). To our further delight, indene could also be used as substrate to afford the corresponding β-aminophosphonates **3z** in moderate yield and with a high dr (57%, dr > 20:1). If we selected the aliphatic alkene of 1-heptane (**3az**) to carry out this difunctionalization, reaction didn't work for the formation of cation intermediate is difficult.

Table 3. The investigation of scope of substrates[a,b]



3a: R^1 = Me, 74%, dr > 20:1
3b: R^1 = H, 67%
3c: R^1 = Et, 62%, dr = 12:1
3d: R^1 = Cpropyl, 70%, dr > 20:1
3e: R^1 = ^{n}-Bu, 51%, dr = 12:1
3f: R^1 = Isoamyl, 57%, dr = 12:1
3g: R^1 = CH_2NHTs, 45%, dr =17:1

3h: R^2 = Me, 71%, dr = 4:1
3i: R^2 = F, 71%, dr = 5:1
3j: R^2 = Cl, 82%, dr = 7:1
3k: R^2 = Br, 72%, dr = 7:1
3l: R^2 = CN, 47%, dr = 2:1
3m: R^2 = CF_3, 29%, dr = 8:1
3n: R^2 = BPin, 40%, dr = 13:1

3o: R^2 = Me, 63%, dr = 16:1
3p: R^2 = Cl, 67%, dr = 20:1
3q: R^2 = Br, 72%, dr > 20:1
3r: R^2 = OAc, 63%, dr = 16:1

3s: R^2 = Me, 63%, dr = 5:1
3t: R^2 = Br, 56%, dr > 20:1
3u: R^2 = Ph, 65%, dr > 20:1

3v: 47%, dr = 9:1

3w: 57%, dr = 15:1

3x: 73%, dr > 20:1

3y: 78%, dr > 20:1

3z: 57%, dr > 20:1

3az: N.R.

[a] Reaction conditions: a solution of **1** (0.6 mmol), **2** (0.4 mmol), and *fac*-Ir(ppy)$_3$ (0.002 mmol, 0.5 mol %) in CH_3CN (1.60 mL) was irradiated by a 5 W blue LED lamp at rt for 8 h. [b] Isolated yield. [c] N.R. is not reaction.

To highlight the synthetic value of our photoredox catalysis protocol, more complex alkenes were used as the substrates (**Scheme 2**). To our delight, some natural conjugated dienes, such as (–)-α-phellandrene and (+)-α-limonene reacted successfully under the optimized conditions: i.e., bifunctional 1,4-aminophosphinoylated chiral products **3aa** and **3ab** were obtained in 51% and 55% yields, respectively. When using the endocyclic groups of (–)-α-pinene and (+)-β-pinene, and adding 2.0 equiv water to the reaction, radical migration led to ring opening and afforded corresponding secondary aminophosphonates in moderate yields (**3ac**, 51%; **3ad**, 60%). Add H_2O in the reaction maybe conducived to ring opening. When using 8-phenyloct-7-enenitrile as the substrate in dioxane, the terminal nitrile could also be used as the nucleophile to afford the macrocyclic lactamide **3ae** in 57% moderate yield with dr = 5:1. Notably, cyclopenta[a] phenanthrene (a steroid) and esterified lovastatin (a drug) could also be modified by this radical phosphorylation; β-benzoxyphosphonates of **3af** and **3ag** were obtained in 47% and 51% yields, respectively. These reactions all exhibited excellent regioselectivity and stereoselectivity, which highlight the synthetic value of our photoredox catalysis protocol.

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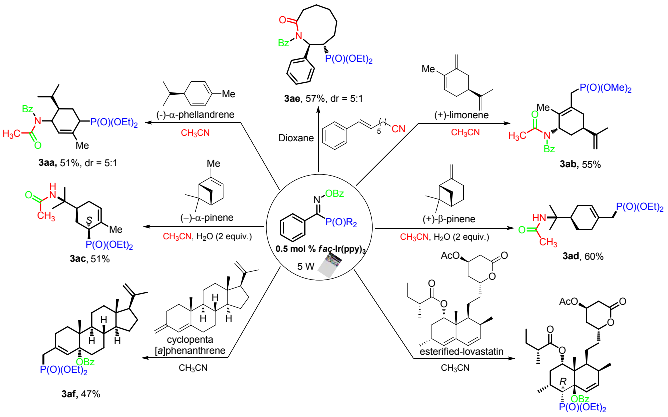
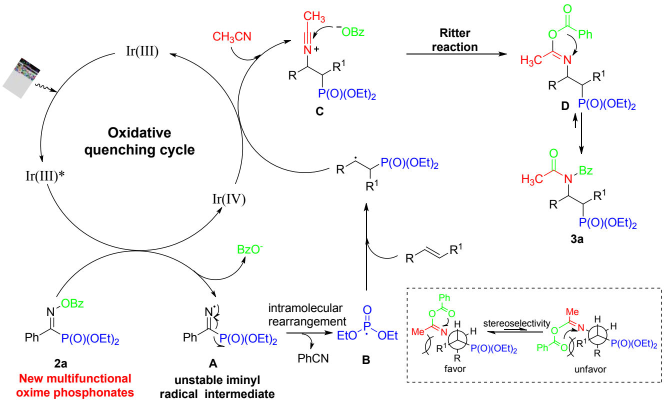


Scheme 2. Different photo-catalyzed phosphorus-radical involved in difunctionalization of alkenes

In order to obatin pivotal informations about the mechanism, we have done some control experiments which including radical traping and deuterium-labeled acetonitrile (details see supporting information). Moreover, to further testify new type of oxime phosphonates could impelled photocatalytic cycle of *fac*-Ir(ppy)$_3$, we have also done the luminescence quenching and cyclic voltammerty (CV) experiments under the model reaction condition respectively (details see supporting information). Considering the results of our experiments and the reported literature,[14] a plausible mechanism is proposed for this transformation (**Scheme 3**). Initially, the excited state *Ir(III) photocatalyst, excited by the blue LED irradiation, is capable of reducing the phosphine source **2a**, to generate the highly reactive Ir(IV) complex and *N*-centered iminyl radical intermediate **A**, with the release of a



Scheme 3. Proposed reaction mechanism

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benzoxyl anion. The iminyl radical A undergoes an β-fragmentation reaction to afford the phosphorus radical **B**.[15] Here, the styrene **1a** can act as a radical acceptor to capture the phosphorus radical by delivering the benzyl radical. Subsequently, regeneration of the ground state photocatalyst results from reduction by the benzyl radical to afford benzyl cation immediately attacked by acetonitrile to the final benzyl nitrilium cation intermediate **C** with completing the catalytic cycle. Finally, the nitrilium cation **C** is attacked by the benzoxyl anion, followed by an acyl migration, to afford the β-aminophosphinoylation product **3a** through a Ritter-type reaction.[7]

In conclusion, we have discovered a new application of phosphorus reagent of oxime phosphonate, which was successfully used for the intermolecular cascade radical addition reaction of alkenes to form β-aminophosphonates via visible-light-driven *N*-centered iminyl radical-mediated and redox-neutral selective C–P bond cleavage in an active phosphorus radical route. This strategy tolerates a wide range of alkenes. It enables the highly selective formation of various chemical bonds in a single step.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 For selected examples, see: (a) T. Koike, M. Akita, *Acc. Chem. Res.* 2016, **49**, 1937. (b) G.-Y. Yin, X. Mu, G.-S. Liu, *Acc. Chem. Res.* 2016, **49**, 2413. (c) T. Koike, M. Akita, *Chem.* 2018, **4**, 409. (d) X.-W. Lan, N.-X. Wang, Y. Xing, *Eur. J. Org. Chem.* 2017, **39**, 5821. (e) S. R. Chemler, M. T. Bovino, *ACS Catal.* 2013, **3**, 1076. (f) Q. Wei, J.-R. Chen, X.-Q. Hu, X.-C. Yang, B. Lu, W.-J. Xiao, *Org. Lett.* 2015, **17**, 4464. (g) R. Sakae, K. Hirano, M. Miura, *J. Am. Chem. Soc.* 2015, **137**, 6460. (h) Q.-X. Qin, Y.-Y. Han, Y.-Y. Jiao, S.-Y. Yu, *Org. Lett.* 2017, **19**, 2909. (i) K. Muniz, L. Barreiro, R. M. Romero, C. Martinez, *J. Am. Chem. Soc.* 2017, **139**, 4354. (j) Y. Cheng, C. Muck-Lichtenfeld, A. Studer, *J. Am. Chem. Soc.* 2018, **140**, 6221. (k) J.-J. Yu, Z. Wu, C. Zhu, *Angew. Chem., Int. Ed.* 2018, **57**, 17156. (l) J. Hou, A. Ee, H. Cao, H.-W. Ong, J.-H. Xu, J. Wu, *Angew. Chem., Int. Ed.* 2018, **57**, 17220. (m) E. D. McCoy, T. Feo, T. A. Harvey, R. O. Prum, *Nat. Commun.* 2018, **9**, 1. (n) K. M. Nakafuku, S. C. Fosu, D. A. Nagib, *J. Am. Chem. Soc.* 2018, **140**, 11202. (o) A. Barthelemy, B. Tuccio, E. Magnier, G. Dagousset, *Angew. Chem., Int. Ed.* 2018, **57**, 13790. (p) S. Jin, O. V. Larionov, *Chem.* 2018, **4**, 1205. (q) N. Otomura, Y. Okugawa, K. Hirano, M. Miura, *Org. Lett.* 2017, **19**, 4802. (r) N. Otomura, Y. Okugawa, K. Hirano, M. Miura, *Synthesis* 2018, **50**, 3402. (s) N. Otomura, K. Hirano, M. Miura, *Org. Lett.* 2018, **20**, 7965. (t) Y. Yuan, Y. Chen, S. Tang, Z. Huang, A. Lei, *Sci. Adv.* 2018, **4**, DOI: 10.1126/sciadv.aat5312. (u) L. Zhang, G. Zhang, P. Wang, Y. Li, A. Lei, *Org. Lett.* 2018, **20**, 7396. (v) Y. Yuan, Y. Cao, Y. Lin, Y. Li, Z. Huang, A. Lei, *ACS Catal.*, 2018, **8**, 10871.

2 For selected examples, see: (a) Y.-M. Li, M. Sun, H.-L. Wang, Q.-P. Tian, S.-D. Yang, *Angew. Chem., Int. Ed.* 2013, **52**, 3972. (b) S.-F. Zhou, D.-P. Li, K. Liu, J.-P. Zou, O. T. Asekun, *J. Org. Chem.* 2015, **80**, 1214. (c) Y. Gao, X. Li, W. Chen, G. Tang, Y.-F. Zhao, *J. Org. Chem.* 2015, **80**, 11398. (d) W. Kong, E. Merino, C. Nevado, *Angew. Chem., Int. Ed.* 2014, **53**, 5078. (e) Y.-Z. Gao, X.-Q. Li, J. Xu, Y.-L. Wu, W.-Z. Chen, G. Tang, Y.-F. Zhao, *Chem. Commun.* 2015, **51**, 1605. (f) H.-Y. Zhang, L.-L. Mao, B. Yang, S.-D. Yang, *Chem. Commun.* 2015, **51**, 4101. (g) J.-A. Li, P.-Z. Zhang, K. Liu, A. Shoberu, J.-P. Zou, W. Zhang, *Org. Lett.* 2017, **19**, 4704. (h) P.-Z. Zhang, L. Zhang, J.-A. Li, A. Shoberu, J.-P. Zou, W. Zhang, *Org. Lett.* 2017, **19**, 5537.

3 For selected examples, see: (a) K. Luo, W.-C. Yang, L. Wu, *Asian, J. Org. Chem.* 2017, **6**, 350. (b) C.-X. Li, D.-S. Tu, R. Yao, H. Yan, C.-S. Lu, *Org. Lett.* 2016, **18**, 4928. (c) L.-L. Liao, Y.-Y. Gui, X.-B. Zhang, G. Shen, H.-D. Liu, W.-J. Zhou, J. Li, D.-G. Yu, *Org. Lett.* 2017, **19**, 3735. (d) C.-H. Wang, Y.-H. Li, S.-D. Yang, *Org. Lett.* 2018, **20**, 2382.

4 For selected examples, see: (a) M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* 2016, **81**, 6898. (b) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* 2016, **116**, 10035. (c) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* 2013, **113**, 5322. (d) J. Xuan, W.-J. Xiao, *Angew. Chem., Int. Ed.* 2012, **51**, 6828. (e) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev.* 2011, **40**, 102.

5 T.-I. Chudakova, Y.-V. Rassuakanaya, A.-A. Sinitsa, P.-P. Onyśko, *Russ. J. Gen. Chem.* 2009, **79**, 195.

6 For selected examples, see: (a) H. Jiang, X. An, K. Tong, T. Zheng, Y. Zhang, S. Yu, *Angew. Chem., Int. Ed.* 2015, **54**, 4055. (b) H.-B. Yang, S. R. Pathipati, N. Selander, *ACS Catal.* 2017, **7**, 8441. (c) E. M. Dauncey, S. P. Morcillo, J. J. Douglas, N. S. Sheikh, D. Leonori, *Angew. Chem., Int. Ed.* 2018, **57**, 744. (d) X.-Y. Yu, Q.-Q. Zhao, J. Chen, J.-R. Chen, W.-J. Xiao, *Angew. Chem., Int. Ed.* 2018, **57**, 15505. (e) X.-Y. Yu, J.-R. Chen, P.-Z. Wang, M.-N. Yang, D. Liang, W.-J. Xiao, *Angew. Chem., Int. Ed.* 2018, **57**, 738.

7 (a) J.-J. Ritter, P.-P. Minieri, *J. Am. Chem. Soc.* 1948, **70**, 4045. (b) A. G. Martínez, R. M. Alvarez, E. T. Vilar, A. G. Fraile, M. Hanack, L. R. Subramanian, *Tetrahedron Lett.* 1989, **30**, 581. (c) K. Kiyokawa, T. Watanabe, L. Fra, T. Kojima, S. Minakata, *J. Org. Chem.* 2017, **82**, 11711. (d) C. Feng, Y. Li, X. Sheng, L. Pan, Q. Liu, *Org. Lett.*, 2018, **20**, 6449.

8 F. Palacios, C. Alonso, M. de Los Santos J, *Chem. Rev.* 2005, **105**, 899.

9 J. G. Allen, F. R. Arthenton, M. J. Hall, C. H. Hassall, S. W. Holmes, R. W. Lambert, L. J. Nisbet, P. S. Ringrose, *Nature.* 1978, **272**, 56.

10 (a) W. W. Smith, P. A. Bartlett, *J. Am. Chem. Soc.* 1998, **120**, 4622. (b) M. C. Allen, W. Fuhrer, B. Tuck, R. Wade, J. M. Wood, *J. Med. Chem.* 1989, **32**, 1652.

11 R. Hirschmann, A. B. Smith, C. M. Taylor, P. A. Benkovic, S. D. Taylor, K. M. Yager, P. A. Sprengler, S. J. Benkovic, *Science.* 1994, **265**, 234.

12 E. Alonso, E. Alonso, A. Solis, C. del Pozo, *Synlett* 2000, 0698.

13 H. Masaaki, K. Makoto, *Nature.* 1959, **184**, 901.

14 For selected examples, see: (a) J. E. Baxter, P. R. S. Davidson, *Makromol, Chem., Rapid Commun.* 1987, **8**, 311. (b) W. A. Pryor, J.-T. Gu, D. F. Church, *J. Org. Chem.* 1985, **50**, 185. (c) D. Weldon, S. Holland, J. C. Scaiano, *J. Org. Chem.* 1996, **61**, 8544. (d) P. S. Engle, S.-L. He, J. T. Banks, K. U. Ingold, J. Lusztyk, *J. Org. Chem.* 1997, **62**, 1210. (e) T. Courant, G. Masson, *J. Org. Chem.* 2016, **81**, 6945.

15 A. Boto, R. Freire, R. Hernández, E. Suárez, *J. Org. Chem.* 1997, **62**, 2975.

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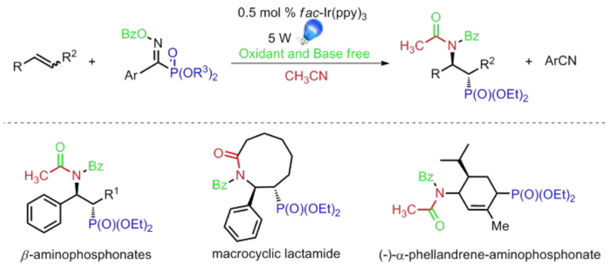

A new oxime phosphonate was firstly synthesized and used in the intermolecular radical addition cascade reaction of alkenes to access β-functionalized phosphonates via visible-light-driven *N*-centered iminyl radical-mediated multiple bond cleavage and recombination process.