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Letter

Cobaloxime Catalysis for Enamine Phosphorylation with Hydrogen Evolution

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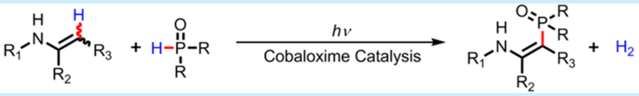
ABSTRACT: Direct phosphorylation of enamine and enamide with hydrogen evolution was realized via cobaloxime catalysis under visible-light irradiation. Control experiments and spectroscopic studies demonstrated a reductive quenching pathway of cobaloxime catalyst to produce phosphinoyl radical, which underwent cross-coupling with various enamines (and enamides) to give diverse β-phosphinoyl products in good to excellent yields. More interestingly, Z/E mixture of acyclic enamines could convert into single Z-products with good reactivity.



Phosphorus-containing complexes are widely applied in biological, pharmaceutical, and material fields.[1] The great demands on its diversity and availability have inspired increasing research efforts of chemists toward efficient and general synthetic routes to its derivatives.[2] Among them, direct cross coupling of β-C (sp^3)−H in enamine with P(O)−H represents a promising and straightforward approach to β-phosphinoyl enamine, which can easily produce diverse downstream phosphorus-containing compounds such as relative ketones and β-amino phosphonic acids.[3] To the best of our knowledge, no enamine substrate has been applied in the above-mentioned transformation, although successful reports based on stoichiometric Mn^{3+},[4] hypervalent iodonium salt,[5] and transition-metal catalysis[6] have realized the β-phosphorylation of enamides in which the nitrogen atom must be protected by one acyl group (or sulfonly group) in the strong oxidative atmosphere. Recently, cobaloxime was found to activate H-phosphine oxide into phosphinoyl radical species under mild conditions,[7] which inspired us to examine the direct phosphorylation of enamine via radical addition by cobaloxime catalysis.[8,9]

To our delight, under visible-light irradiation of catalytic Co(dmgH)$_2$pyCl, different enamines with Z/E mixture coupled with diverse diarylphosphine oxides at room temperature to produce specific Z-β-phosphinoyl enamines irrespective of the electron property and steric hindrance, which was unlocked in previous reports (Scheme 1). Moreover, various enamides were also suitable reactants and exhibited high reactivity. Different from our previous phosphorylation of terminal olefins via intermolecular hydrogen atom transfer process,[7] a cross-coupling hydrogen evolution[10−12] pathway smoothly proceeded without any external oxidative agents or hydrogen acceptors, establishing a general and highly atom-economic method for β-phosphorylation of enamine and enamide.

Initially, 3-phenyl-3-(phenylamino)acrylonitrile (Z/E = 1:1) **1** and diphenylphosphine oxide **2** were selected as model substrates to explore the feasibility of cobaloxime catalysis. With 10 mol % Co(dmgH)$_2$pyCl as catalyst and 1 equiv of pyridine as base in DMF, blue light irradiation for 14 h gave the target product **3** in 7% yield (Table 1, entry 1). Further screen of other solvents including MeOH, MeCN, DCE, DCM showed that DCE and DCM were the highest to afford **3** with 76% and 74% yields relatively (Table 1, entries 2−5). Considering the easy workup, DCM was chosen for the next optimization on photocatalysts. As shown in Table 1, Co^{III} salts (Co(dmgH)$_2$pyCl, Co(dmgH)(dmgH$_2$)Cl$_2$), Co(dmgH)$_2$(4-CO$_2$MePy)Cl) were higher in catalytic ability than Co^{II} (Co(dmgBF$_2$)$_2$(L)$_2$, L = MeCN, H$_2$O) (Table 1, entries 6−9). As for the base, omitting pyridine or replacement by TEA, DABCO, Na$_2$HPO$_4$, or Na$_2$CO$_3$ gave lower conversion yields (Table 1, entry 10; Table S1). Prolonging the reaction time to 48 h provided the highest 93% yield of product **3** (Table 1, entry 11). Control experiments confirmed

Scheme 1. Phosphorylation of Enamine and Enamides

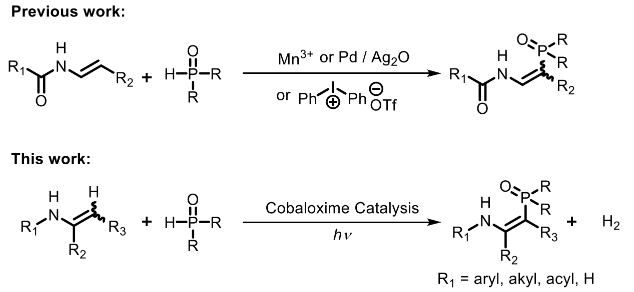


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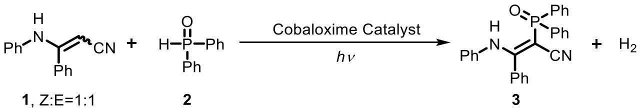
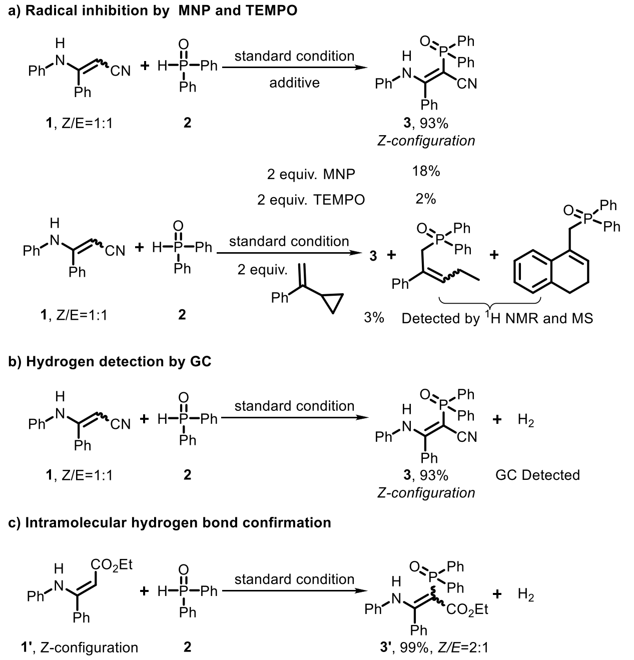
Table 1. Optimization of Reaction Conditions[a]



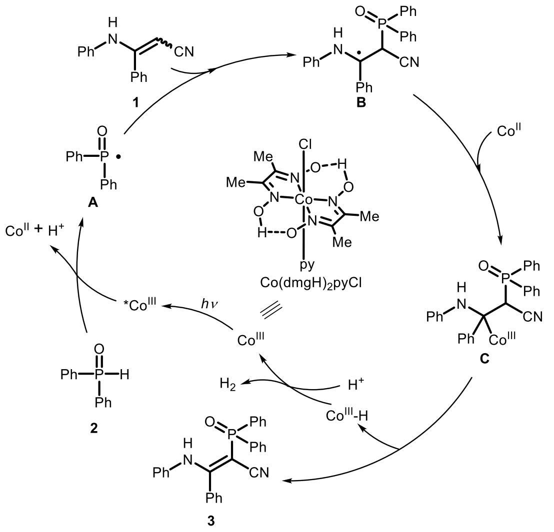
entry	photocatalyst	solvent	yield[b] (%)
1	Co(dmgH)$_2$pyCl	DMF	7
2	Co(dmgH)$_2$pyCl	MeOH	9
3	Co(dmgH)$_2$pyCl	MeCN	51
4	Co(dmgH)$_2$pyCl	DCE	76
5	Co(dmgH)$_2$pyCl	DCM	74
6	Co(dmgH)$_2$(dmgH$_2$)Cl$_2$	DCM	62
7	Co(dmgH)$_2$(4-CO$_2$MePy)Cl	DCM	68
8	Co(dmgBF$_2$)$_2$(H$_2$O)$_2$	DCM	18
9	Co(dmgBF$_2$)$_2$(MeCN)$_2$	DCM	36
10[C]	Co(dmgH)$_2$pyCl	DCM	50
11[d]	Co(dmgH)$_2$pyCl	DCM	93 (86)
12		DCM	0
13[e]	Co(dmgH)$_2$pyCl	DCM	0

[a] Reaction conditions (unless otherwise specified): enamine **1** (0.1 mmol), diphenylphosphine oxide **2** (1.5 equiv, 0.15 mmol), cobaloxime (10 mol %) and pyridine (1.0 equiv, 0.1 mmol) in solvent (2 mL) was irradiated with blue LEDs for 14 h under argon atmosphere at room temperature. [b] ^{31}P NMR yield with triphenylphosphane as internal standard. Isolated yield in parentheses. [C] No pyridine. [d] 48 h. [e] No light.

Scheme 2. Mechanistic Experiments



Scheme 3. Proposed Mechanism



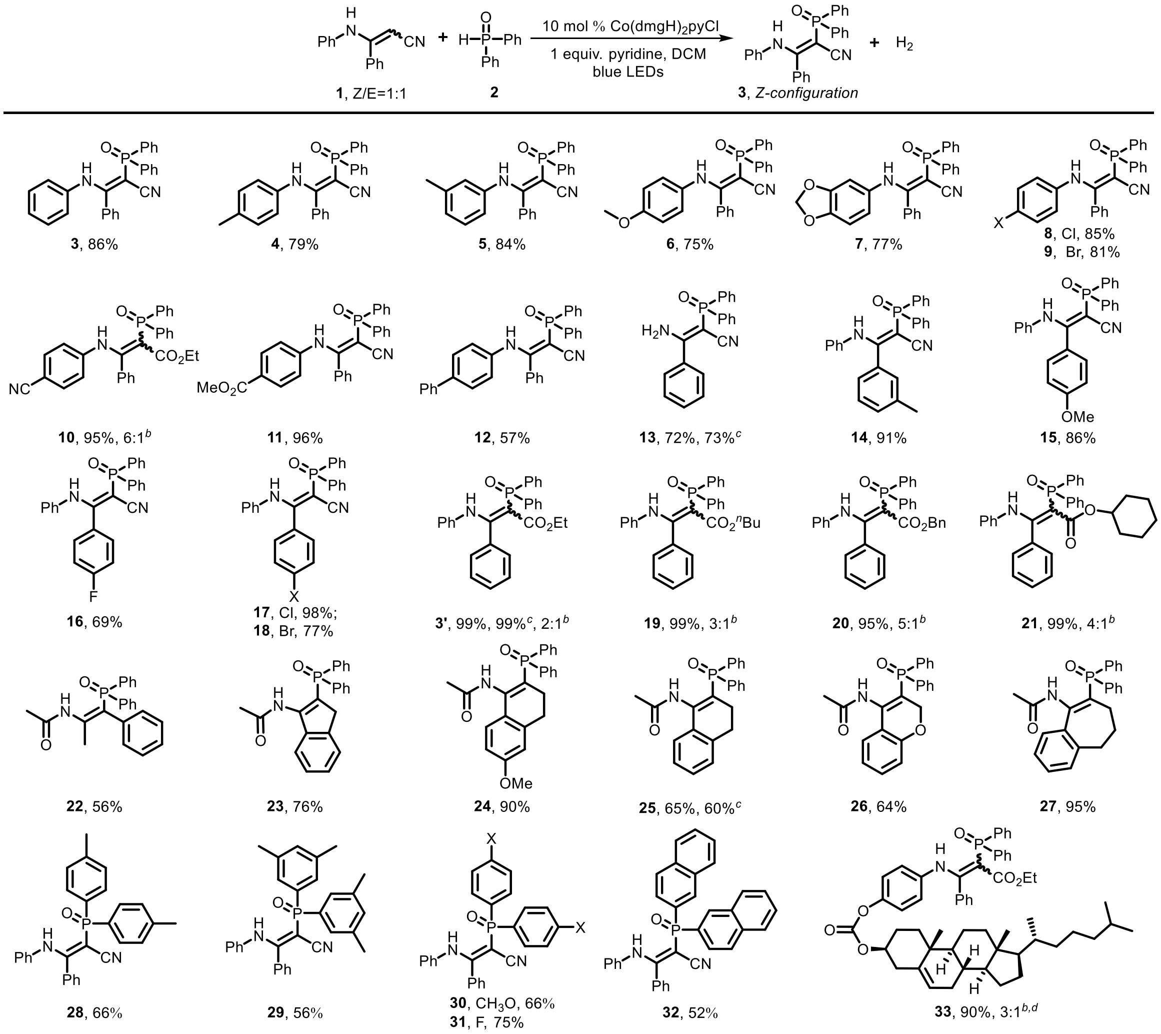
no reaction at all occurred without catalyst or light (Table 1, entries 12 and 13), indicating the nature of photocatalysis.

As only cobaloxime catalyst responds to visible light and other two substrates have no absorption at 450 nm (Figure S1), a new absorption peak between 400 and 500 nm was assigned to Co(II) species after irradiating the system of cobaloxime and diphenylphosphine oxide **2** for 10 min (Figure S2a). Significantly, further addition of enamine into the above-mentioned reaction mixture, in addition to the observable Co(I) signal (Figure S2b),[13] a characteristic signal of phosphinoyl radical[14] was directly obtained by electron-spin resonance (ESR) with 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as radical capture. These results demonstrated that excited cobaloxime catalyst could interact with diphenylphosphine oxide **2** to provide low-valent Co species and phosphinoyl radical. As supported by spectroscopic results, 2-methyl-2-nitrosopropane (MNP) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as radical-trapping agents seriously suppressed the conversion efficiency, and the radical clock reaction with 2 equiv of (1-cyclopropylvinyl)benzene led to the cyclopropane-opening products (Scheme 2a). Furthermore, no external oxidant was needed in our system, and hydrogen gas was detected by gas chromatography rather than hydrogenation of substrate or product (Scheme 2b). As for the *Z*-selectivity of product from *Z*/*E* mixture of acyclic enamine **1**, ethyl (*Z*)-3-phenyl-3-(phenylamino)acrylate **1′** with an ester group was employed to react with diphenylphosphine oxide **2**, which gave a *Z*/*E* (2:1) mixture of product **3′** with 99% yield (Scheme 2c). This result revealed the high selectivity probably arised from the intramolecular hydrogen-bond effect between N−H and phosphinoyl group in the product.

On the basis of the above experimental results, a rational mechanism was proposed as listed in Scheme 3. Under visible-light irradiation, photoexcited cobalt(III) oxime oxidized diphenylphosphine oxide **2** into phosphinoyl radical **A** with the formation of Co(II) species. Generated electrophilic intermediate **A** was then added to the C═C bond of enamine to form carbon radical **B** adjacent to nitrogen atom, which direct coupled with Co (II) to form C−Co(III) intermediate (**C**). Via *β*-H elimination, the product **3** was obtained accompanyed by the formation of Co(III)−H. Co(III)−H reacted with another proton to release hydrogen and regenerate cobalt(III), completing the reaction circle. In this process, the possibility of either single electron transfer between Co(II) and intermediate **B** to final product **3** and Co(I) which captured one proton to generate Co(III)−H, or the direct hydrogen abstract by Co(II) from intermediate **B** to produce **3** and Co(III)−H could not be completely excluded.[10c]

With the understanding of mechanism in mind, more efforts were focused on the generality of this cobaloxime catalysis for enamine phosphorylation. Various enamines even enamides

Scheme 4. Scope of Enamine and Enamide[a]



[a]Reaction condition (unless otherwise specified): enamine (*Z*/*E* = 2:1−1:2) or enamide (0.1 mmol), diarylphosphine oxide (1.5 equiv, 0.15 mmol), Co(dmgH)$_2$pyCl (10 mol %) and pyridine (0.1 mmol) in DCM (2 mL) was irradiated with blue LEDs for 48 h under argon atmosphere at room temperature. **10**, **13**, **3′**, and **19**−**20** came from *Z*-enamine substrates. [b]*Z*/*E* value was detected via ^{31}P NMR spectra. [c]1 mmol reaction. [d]Reaction time was 22 h.

were examined to react with diarylphosphine oxides. As shown in Scheme 4, analysis of the results gave the following conclusions: (1) Both electron-donating and -withdrawing substitution on the *N*-aryl group showed good tolerance (**3**−**11**). Good to excellent yields were obtained in which a strong electron-deficient ester substrate could afford 96% yield of products (**10**). *P*- and *m*-methyl enamines gave relative products in 79% and 84%, showing little steric effect (**4**, **5**). In addition, larger conjugated 4-phenyl substitution (**12**) and simple NH$_2$ (**13**) all were competent to react smoothly and exhibited good reactivity. As for the α position of enamine, variations on the arene moiety including 3-methyl (**14**), 4-methoxyl (**15**), 4-fluoro (**16**), 4-chloro (**17**), and 4-bromo (**18**) substitutions were facile to produce β-phosphinoyl enamines with 69−98% yields. It should be highlighted that all these products were single *Z* configurations from enamines with a *Z*/*E* mixture (*Z*/*E* = 2:1−1:2), except **10** and **13** from *Z*-substrates. (2) In terms of the β-substitution, besides CN, other groups like esters gave excellent reaction tolerance. Ethyl (**10**, **3′**), butyl (**19**), benzyl (**20**),and even cyclohexyl (**21**) esters all gave ≥95% yield of products albeit with a low *Z*/*E* ratio, due to the competition of intramolecur hydrogen bond between N−H···(O)P and N−H···(O)C. (3) In order to extend the synthetic application of this method, linear and cyclic enamides were further tested (**22**−**27**). *N*-(1-Phenylprop-1-en-2-yl)acetamide with a methyl group in the α-position gave moderate yield (**22**). Enamides derived from various benzocyclic ketones such as 2,3-dihydro-1*H*-inden-1-one (five-membered, **23**), 3,4-dihydronaphthalen-1(2*H*)-one (six membered, **24**, **25**), chroman-4-one (six membered, **26**), and 6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-5-one (seven membered, **27**) were suitable reactants to produce the corresponding products in 65%−95% yields. (4) In terms of reaction partner, diarylphosphine oxide with alkyl, alkoxyl, and halogen substitutions all exhibited good reactivity (**28**−**31**). Di(naphthalen-2-yl)phosphine oxide bearing a large hindrance could also react with 3-phenyl-3-(phenylamino)acrylonitrile (*Z*/*E* = 1:1) and afforded 52% yield with single *Z* isomer (**32**). (5) In order to further explore the practicality of this method, scale-up reaction of 3-amino-3-phenylacrylonitrile, ethyl (*Z*)-3-phenyl-3-(phenylamino)acrylate, and *N*-(3,4-dihydronaphthalen-1-yl)acetamide in 1 mmol were carried out to afford the target products **13**, **3′**, and **25** in 73%, 99%, and 60% yields with almost no loss in yield. The complex cholesterol derivative was also feasible to give the target product with 90% yield (**33**). All of the results revealed the great potential of cobaloxime catalysis for synthetic application.

In conclusion, we have successfully realized the phosphorylation of enamine and enamide via cobaloxime catalysis. Under visible-light irradiation, different functionalized enamines and enamides showed good reactivity to reaction with diverse H-phosphine oxides, providing valuable added *β*-phosphinoyl products with no external oxidant or hydrogen atom acceptors. The proton and electron were confirmed to couple into hydrogen, revealing the great advantages on reaction simplicity and atom-economy. Furthermore, the selective specificity for *Z*-isomer product in some enamines conversion, highlighting the accurate application of intramolecular hydrogen bond in chemical transformation. The features of mild reaction conditions, good functional group tolerance, and conversion yields make this strategy a promising alternative for the construction of *β*-phosphinoyl enamines and enamides, which could be further employed into the last-stage decoration of complex molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01709.

> Experimental procedure, spectroscopic data, characterization of all products, and copies of ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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