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Aerobic Oxidative Carbonylation of Enamides by Merging Palladium with Photoredox Catalysis

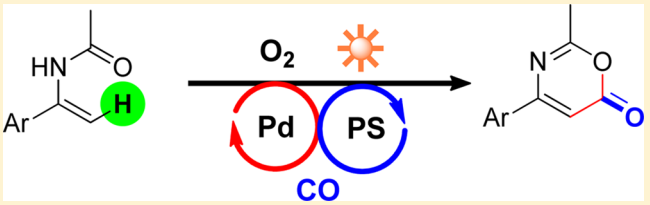
Kun Liu,[†] Minzhu Zou,[†] and Aiwen Lei*[,†,‡]

[†]College of Chemistry and Molecular Sciences, the Institute for Advanced Studies (IAS), Wuhan University, Wuhan 430072, China

[‡]State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

Supporting Information

ABSTRACT: Intramolecular oxidative carbonylation reaction is an efficient approach for constructing heterocycles. However, stoichiometric amount of hypervalent metal salts is usually required in this transformation. Here we show an aerobic intramolecular oxidative carbonylation of enamides by combining palladium and photoredox catalysis. The dual catalytic system enables oxygen directly as oxidant, which provides a mild and environmentally friendly method for the synthesis of 1,3-oxazin-6-ones.

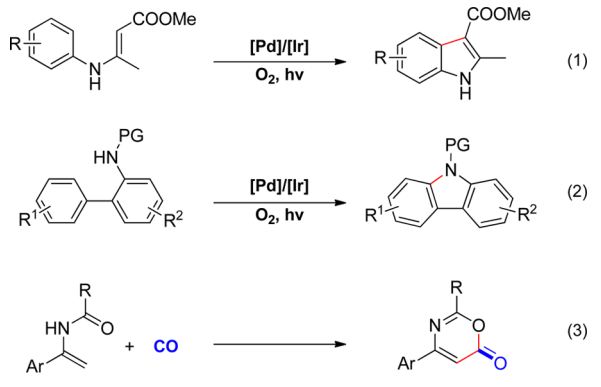


INTRODUCTION

Heterocyclic compounds are one of the most important kinds of structural motif and are widely used in medicine, pesticides, materials, and other fields.[1] Consequently, intense efforts have been made to exploit more preferable routes for their syntheses. Over the past decade, transition-metal-catalyzed intramolecular carbonylation via C−H bond activation with carbon monoxide has emerged as an important approach to construct heterocyclic molecules.[2] For numerous C−H carbonylation reactions to synthesize heterocyclic structures reported to date, the use of large amounts of hypervalent metal salts such as copper(II) salts is a general feature of these transformations, because the in situ generated metal complex needs to be reoxidized first before the next catalytic cycle. This feature hinders the general application of its transformation. Thus, an environmentally friendly catalytic system is required to be developed to deal with this issue.

Recently, photoredox catalysis has attracted substantial attention in fulfilling many kinds of new transformations due to its great compatibility and versatility.[3] It was discovered that single electron transfer (SET) processes could be utilized for the oxidation of transition-metal complex intermediates, which was promoted by visible light.[4] In 2014, using O_2 as sole oxidant, Rueping and co-workers disclosed C−H olefination through combined palladium and photoredox catalysis enabling the synthesis of indoles (Scheme 1, eq 1).[4f] Then, the group of Cho has successfully developed the construction of carbazoles through a dual catalysis system of palladium and photoredox catalysis (Scheme 1, eq 2).[5] In these processes, photoredox catalysis has played the role of mediating the electron transfer process between the palladium intermediate and oxygen. And in 2013, Guan and co-workers achieved palladium-catalyzed oxidative carbonylation of enamides with equivalent $Cu(OAc)_2$ as oxidant (Scheme 1, eq 3).[6] Based on recent results on the

Scheme 1. Aerobic Oxidative Annulation by Merging Palladium with Photoredox Catalysis



Guan's Work: 5 mol% $Pd(OAc)_2$, 1 equiv $Cu(OAc)_2$
This Work: 5 mol% $Pd(OAc)_2$, 1 mol% $Ru(bpy)_3Cl_2$, blue LEDs, O_2

combination of palladium and photoredox catalysis,[4a,f,h,5,7] we wondered whether the recyclization of metal catalyst in the oxidative carbonylation reaction could be successfully accomplished by a photoredox process. In this work, we communicate our recent progress on aerobic oxidative carbonylation of enamides for the synthesis of 1,3-oxazin-6-ones by merging palladium with photoredox catalysis (Scheme 1, eq 3).

On the basis of the widely accepted mechanism of palladium catalysis and photoredox catalysis,[1,2,3b,d,8] an aerobic oxidative intramolecular carbonylation of enamides can be assumed to proceed through the following steps shown in Scheme 2. First,

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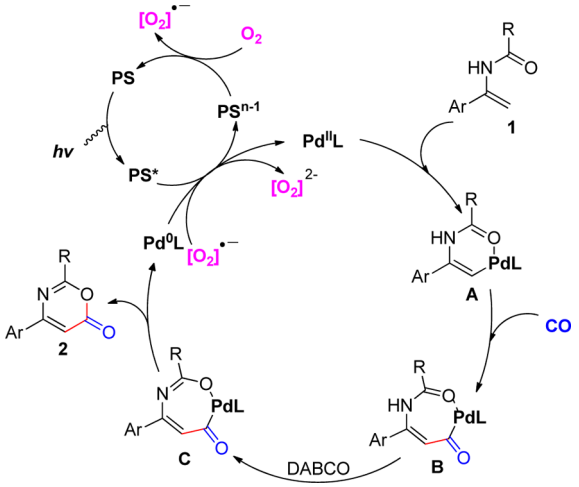
Scheme 2. Proposed catalytic Cycles for the Aerobic Oxidative Carbonylation of Enamides

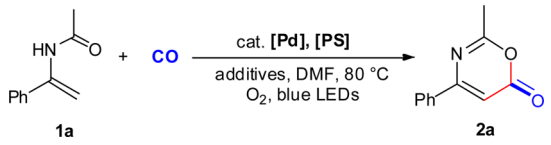


alkenyl C−H activation by $Pd(OAc)_2$ forms the vinylpalladium intermediate A. Coordination and insertion of CO into A affords the acylpalladium intermediate B. Then, B is transformed into C assisted by DABCO. Reductive elimination of C gives the carbonylation product **2a** and Pd^0. After being excited by light irradiation, the photoredox catalyst is capable of oxidation by electron transfer, thus regenerating the catalytically active Pd^{II} species. The superoxide anion itself may then oxidize the Pd^0 by accepting an electron. A catalytic amount of photoredox catalyst in the presence of visible light could facilitate the reoxidation of the Pd catalyst, thereby obviating the use of an excess of metal salts. According to Guan's work, additives were also important. Adding KI into the reaction system could improve the efficiency of palladium-catalyzed oxidative carbonylation reaction through coordination. And Ac_2O was believed to inhibit the possible reduction of the active palladium(II) catalyst intermediate to inactive palladium(0) by CO.

RESULTS AND DISCUSSION

We started our experiment by using O_2 solely as oxidant in the oxidative carbonylation of *N*-(1-phenylvinyl)acetamide (**1a**). Trace amount of the desired product could be obtained only with palladium catalyst (Table 1, entry 1). This result indicated that oxygen solely was unable to facilitate the recycling of the palladium catalyst. Then in order to test our hypothesis, we tried to screen a number of photoredox catalysts. To our delight, when we applied 1 mol % of $RuCl_2(bpy)_3$ into the system (Table 1, entry 7), the reaction yield was improved to 51%. Meanwhile, only a trace amount of the product could be obtained when the reaction was carried out in the dark, which indicated that both photoredox catalyst and light were essential for this transformation (Table 1, entry 13). Increasing the electron density through sequential introduction of Me groups on the bipyridine backbone led to a drop in the yield from 51% to 47% (Table 1, entry 6). Using the more strongly oxidizing $Ru(bpz)_3(PF_6)_2$, only 25% of product could be obtained. When iridium photocatalysts were used, low yields were obtained, whether electron-rich or -poor ligands were used (Table 1, 2−4). This finding indicated that radical oxo species[9] were not directly involved in the palladium complex oxidation, since both $[Ru(bpy)_3]^{2+}$ and the corresponding iridium complexes were known to generate reactive oxygen intermediates. Furthermore,

Table 1. Optimization of the Catalysis System[a]



1a 2a

entry	[Pd]	PC	yield[b] (%)
1	$Pd(OAc)_2$		trace
2	$Pd(OAc)_2$	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	25
3	$Pd(OAc)_2$	$Ir(dFppy)_2(phen)PF_6$	19
4	$Pd(OAc)_2$	$Ir(ppy)_2(dtbbpy)PF_6$	32
5	$Pd(OAc)_2$	$Ru(bpz)_3(PF_6)_2$	25
6	$Pd(OAc)_2$	$Ru(p\text{-}Mebpy)_3Cl_2$	47
7	$Pd(OAc)_2$	$Ru(bpy)_3Cl_2$	51
8	$Pd(OAc)_2$	$Acr^+Mes\ ClO_4^-$	25
9[c]	$Pd(OAc)_2$	eosin Y	12
10	$PdCl_2$	$Ru(bpy)_3Cl_2$	35
11	$PdCl_2(CH_3CN)_2$	$Ru(bpy)_3Cl_2$	42
12	$Pd_2(dba)_3$	$Ru(bpy)_3Cl_2$	19
13[d]	$Pd(OAc)_2$	$Ru(bpy)_3Cl_2$	trace

[a]Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), $Ru(bpy)_3Cl_2$ (1 mol %), additives Ac_2O (0.6 mmol), DABCO (0.6 mmol), and KI (0.075 mmol), a balloon filled with CO/O_2 (7:1) in DMF (2.0 mL), 80 °C, under the irradiation of 3 W blue LEDs for 6 h. [b]Yields are determined by GC analysis with biphenyl as the internal standard. [c]Green LEDs were used instead. [d]In the dark.

poor yield was observed when a catalytic amount of either *N*-Me-9-mesityl acridinium or eosin Y was applied as the photoredox catalyst (Table 1, entry 8, 9). In the next step, efforts were made to optimize the choice of palladium catalyst. First, when $PdCl_2$ and $PdCl_2(MeCN)_2$ were used instead of $Pd(OAc)_2$, lower yields were obtained (Table 1, entry 10, 11). And $Pd_2(dba)_3$ showed poor reactivities in this transformation, which indicated the importance of choosing a suitable Pd complex (Table 1, entry 12).

For further improvement of the reaction efficiency, phosphine ligands were then screened in combination with $Pd(OAc)_2$ as the catalyst precursor. To our delight, when we applied 16 mol % of PPh_3 into the system, the reaction yield was improved to 62% (Table 2, entry 1). However, other monophosphine ligands like PCy_3 showed poor reactivity and furnished the desired product in 38% yield (Table 2, entry 2). When we changed monodentate ligands to bidentate ligands, it seemed that the bite angle of the bis(phosphine) ligand had great influence in the transformation (Table 2, entry 3−9). Ligands dppe or dppp resulted in low conversion into the desired product. To our delight, when large bite angle ligands like dppb, dppen, and dpph were added, the yield was improved to more than 60%. Further increase of the steric bulk and bite angle by using DPEphos showed similar efficiency. However, 8 mol % Xantphos led to a substantial increase in catalytic activity, and the desired carbonylation product **2a** was isolated in 82% yield (Table 2, entry 9). Then in order to explore the fate of the phosphine ligand under the oxidative conditions, ^{31}P NMR detection experiment of the reaction system revealed that the ligands would transfer into the oxidized product during the reaction process. We speculated that the oxidized phosphine ligands were the active species for facilitating this transformation (Figure S1).[10]

After considerable efforts, we found that the combination of $Pd(OAc)_2$ and $Ru(bpy)_3Cl_2$ could obtain a very high yield with

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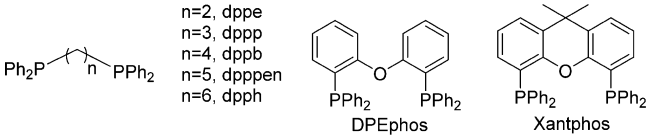
Table 2. Screening of Different Ligands[a]

1a 2a

entry	ligand	yield[b] (%)
1	16 mol % PPh_3	62
2	16 mol % PCy_3	38
3	8 mol % dppe	trace
4	8 mol % dppp	17
5	8 mol % dppb	62
6	8 mol % dpppen	69
7	8 mol % dpph	65
8	8 mol % DPEphos	69
9	8 mol % Xantphos	82

[a]Reaction conditions: **1a** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), $Ru(bpy)_3Cl_2$ (1 mol %), 16 mol % for monodentate lignads, 8 mol % for bidentate ligands, additives Ac_2O (0.6 mmol), DABCO (0.6 mmol), and KI (0.075 mmol), a balloon filled with CO/O_2 (7:1) in DMF (2.0 mL), 80 °C, under the irradiation of 3 W blue LEDs for 6 h. Ligand structures:

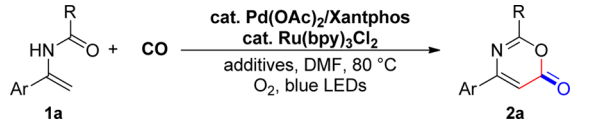


[b]Yields are determined by GC analysis with biphenyl as the internal standard.

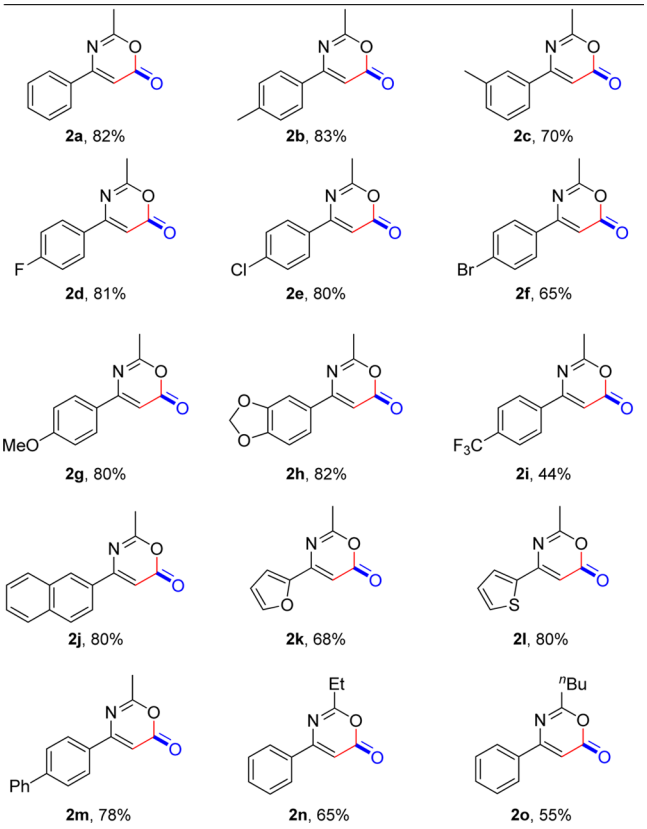
N-(1-phenylvinyl)acetamide as substrate under mild conditions. Since good results were achieved, we turned to explore the synthetic application of this dual catalytic system in the synthesis of 1,3-oxazin-6-ones under the standard conditions. Aryl enamides with methyl group such as *p*-methyl and *m*-methyl could give the desired product in 83% and 70% yields, respectively (Table 3, **2b, 2c**). Notably, halide substituents on the aromatic ring were well tolerated in this transformation and afforded moderate to good yield (Table 3, **2d−2f**). Electron-donating substituted enamides such as methoxyl and [1,3]-dioxale both could provide very good yields (Table 3, **2g** and **2h**). Moreover, a 44% yield was obtained when using strong electron-withdrawing substituent like trifluoromethyl on the benzene ring of the enamide (Table 3, **2i**). Other kinds of aromatic rings such as *β*-naphthyl, furan, thiophen, and biphenyl were also tested in this transformation, and they all demonstrated good reaction efficiency (Table 3, **2j−2m**). As for other types of *N*-acetyl substituted enamides, *N*-propionyl and *N*-pentanyl enamides were also investigated to explore the reaction scope and proceeded smoothly to give the corresponding 2-ethyl- and 2-butyl-1,3-oxazin-6-ones in moderate yields (Table 3, **2n** and **2o**).

To demonstrate the reaction efficiency of this combined catalysis system, we tried to expand the reaction to a 3 mmol scale. In the case of **1a**, a good reaction selectivity and yield could still be obtained (Scheme 3). Obviously, this was a great advantage of this combined catalysis system over the process with equivalent $Cu(OAc)_2$ as oxidant according to the demand for atom-economical and sustainable chemistry.

Table 3. Substrate Scope of the Oxidative Carbonylation[a]

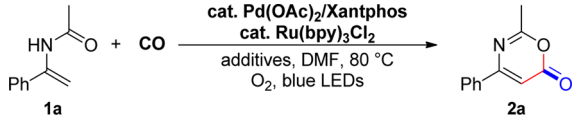


1a 2a



[a]Reaction conditions: **1** (0.2 mmol), $Pd(OAc)_2$ (5 mol %), $Ru(bpy)_3Cl_2$ (1 mol %), Xantphos (8 mol %), additives Ac_2O (0.6 mmol), DABCO (0.6 mmol), and KI (0.075 mmol), a balloon filled with CO/O_2 (7:1) in DMF (2.0 mL), 80 °C, under the irradiation of 3 W blue LEDs for 6 h. Yield refers to isolated yield.

Scheme 3. Gram Scale Reaction[a]



1a 3 mmol 2a 77%, 0.43 g

[a]Reaction conditions: **1a** (3 mmol), $Pd(OAc)_2$ (5 mol %), $Ru(bpy)_3Cl_2$ (1 mol %), Xantphos (8 mol %), addivives Ac_2O (9 mmol), DABCO (9 mmol), and KI (1.125 mmol), a balloon filled with CO/O_2 (7:1) in DMF (30 mL), 80 °C, under the irradiation of 3 W blue LEDs for 24 h.

CONCLUSION

In conclusion, we have reported a combination of photoredox and metal catalysis for the oxidative carbonylation of enamides by C−H activation. The unique interaction between metal and photoredox catalysis allowed the direct reoxidation of the metal catalyst. Moreover, Xantphos as ligand can also promote the transformation. The strategy employed in this study, which combined photoredox with transition metal catalysis avoided the utilization of stoichiometric amounts of harsh or potentially toxic oxidants. Also with very good functional group tolerance,

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this process might be able to be applied in the formation of other environmentally benign reactions.

EXPERIMENTAL SECTION

General Information. All manipulations were carried out using standard Schlenk techniques. All glassware was oven-dried at 120 °C for more than 1 h prior to use. DMF was dried and distilled from 4 Å molecular sieves under nitrogen. Unless otherwise noted, analytical grade solvents and commercially available reagents were used as received. Enamides were prepared according to literature procedures.[11] Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200−300 mesh silica gel in petroleum (bp 60−90 °C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, which are listed below as volume/volume ratios. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and HRMS. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on 400, 101, and 377 MHz instruments, respectively. The chemical shifts (δ) were given in parts per million relative to internal tetramethylsilane (0 ppm for ^{1}H) and $CDCl_3$ (77.0 ppm for ^{13}C). High resolution mass spectra (HRMS) were measured with ESI (LTQ-Orbitrap) or EI (TOF) ionization sources for the molecular ion $(M + H)^+$ or (M^+).

General Procedure for Aerobic Oxidative Carbonylation of Enamides by Merging Palladium with Photoredox Catalysis. Enamide **1** (0.2 mmol), $Pd(OAc)_2$ (5 mol %, 2.2 mg), $RuCl_2(bpy)_3$ (5 mol %, 1.3 mg), KI (0.075 mmol, 12.5 mg), and DABCO (0.6 mmol, 67.2 mg) were added to a 25 mL oven-dried Schlenk tube equipped with a magnetic stirred bar, and a balloon filled with CO/O_2 (7:1) was connected to the Schlenk tube through the side arm and purged three times. DMF (2 mL) and Ac_2O (0.6 mmol, 67.2 mg) were injected into the tube by syringe. The reaction was then stirred at 80 °C and under the irradiation of 3 W blue LEDs (450−480 nm) for 6 h. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature and vented to discharge the excess CO. The reaction was quenched with H_2O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding 1,3-oxazin-6-one **2** with hexane/ethyl acetate as the eluent (30/1).

*2-Methyl-4-phenyl-6H-1,3-oxazin-6-one (**2a**):*[6] white solid (30.7 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.2 Hz, 2H), 7.71−7.39 (m, 3H), 6.53 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 161.5, 160.2, 134.1, 131.8, 128.9, 127.2, 101.7, 21.8.

*2-Methyl-4-(p-tolyl)-6H-1,3-oxazin-6-one (**2b**):*[6] white solid (33.4 mg, 83%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 6.48 (s, 1H), 2.49 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 161.5, 160.3, 142.6, 131.3, 129.6, 127.2, 100.8, 21.8, 21.5.

*2-Methyl-4-(m-tolyl)-6H-1,3-oxazin-6-one (**2c**).* white solid (28.2 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91−7.65 (m, 2H), 7.47−7.29 (m, 2H), 6.50 (s, 1H), 2.49 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 161.6, 160.1, 138.6, 134.0, 132.6, 128.8, 127.8, 124.3, 101.6, 21.7, 21.4. HRMS (EI) calcd for $C_{12}H_{11}NO_2$ $[M]^+$: 201.0790. Found: 201.0792.

*4-(4-Fluorophenyl)-2-methyl-6H-1,3-oxazin-6-one (**2d**):*[6] white solid (33.2 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14−7.82 (m, 2H), 7.28−7.07 (m, 2H), 6.47 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 165.0 (d, J_{C-F} = 252.0 Hz), 160.1 (d, J_{C-F} = 37.6 Hz), 130.2, 129.5 (d, J_{C-F} = 8.9 Hz), 116.0 (d, J_{C-F} = 21.8 Hz), 101.2, 21.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ −107.35.

*4-(4-Chlorophenyl)-2-methyl-6H-1,3-oxazin-6-one (**2e**):*[6] white solid (35.4 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 6.50 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 160.3, 159.9, 138.1, 132.5, 129.2, 128.5, 101.7, 21.8.

*4-(4-Bromophenyl)-2-methyl-6H-1,3-oxazin-6-one (**2f**):*[6] white solid (34.5 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 160.3, 159.8, 133.0, 132.1, 128.7, 126.7, 101.7, 21.8.

*4-(4-Methoxyphenyl)-2-methyl-6H-1,3-oxazin-6-one (**2g**):*[6] white solid (34.7 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.41 (s, 1H), 3.87 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 162.7, 161.0, 160.4, 129.1, 126.4, 114.3, 99.5, 55.4, 21.7.

*4-(Benzo[d][1,3]dioxol-5-yl)-2-methyl-6H-1,3-oxazin-6-one (**2h**):*[6] white solid (37.9 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 1H), 7.42 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H), 6.37 (s, 1H), 6.06 (s, 2H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 160.8, 160.3, 150.9, 148.4, 128.2, 122.8, 108.6, 107.1, 101.8, 100.0, 21.8.

*2-Methyl-4-(4-(trifluoromethyl)phenyl)-6H-1,3-oxazin-6-one (**2i**).* white solid (22.5 mg, 44%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 2H), 6.59 (s, 1H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 159.9, 159.6, 137.5, 133.2 (q, J_{C-F} = 32.9 Hz), 127.6, 125.8 (q, J_{C-F} = 3.8 Hz), 123.6 (q, J_{C-F} = 273.5 Hz), 103.2, 21.8. ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.97. HRMS (EI) calcd for $C_{12}H_8F_3NO_2$ $[M]^+$: 255.0507. Found: 255.0504.

*2-Methyl-4-(naphthalen-2-yl)-6H-1,3-oxazin-6-one (**2j**):*[6] white solid (37.9 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.04−7.80 (m, 4H), 7.56 (m, 2H), 6.62 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 161.1, 160.1, 134.8, 132.9, 131.2, 129.3, 128.7, 128.6, 128.0, 127.7, 126.8, 123.0, 101.7, 21.8.

*2-Ethyl-4-(furan-2-yl)-6H-1,3-oxazin-6-one (**2k**).* white solid (23.0 mg, 68%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 0.8 Hz, 1H), 7.21 (d, J = 3.6 Hz, 1H), 6.58 (dd, J = 3.6, 1.6 Hz, 1H), 6.37 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 159.7, 152.0, 149.8, 146.5, 115.7, 112.8, 98.1, 21.6. HRMS (EI) calcd for $C_9H_7NO_3$ $[M]^+$: 177.0426. Found: 177.0423.

*2-Ethyl-4-(thiophen-2-yl)-6H-1,3-oxazin-6-one (**2l**).* white solid (30.1 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 3.6, 0.8 Hz, 1H), 7.61 (dd, J = 4.8, 0.8 Hz, 1H), 7.18 (dd, J = 5.2, 4.0 Hz, 1H), 6.35 (s, 1H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 159.8, 156.4, 139.4, 131.9, 129.1, 128.9, 98.5, 21.7. HRMS (EI) calcd for $C_9H_7NO_2S$ $[M]^+$: 193.0197. Found: 193.0199.

*4-([1,1′-Biphenyl]-4-yl)-2-methyl-6H-1,3-oxazin-6-one (**2m**):*[6] white solid (41.0 mg, 78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.43−7.37 (t, J = 6.8 Hz, 1H), 6.55 (s, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 161.1, 160.2, 144.5, 139.7, 132.9, 128.9, 128.1, 127.7, 127.5, 127.1, 101.3, 21.8.

*2-Ethyl-4-phenyl-6H-1,3-oxazin-6-one (**2n**):*[6] white solid (26.1 mg, 65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (m, 2H), 7.60−7.42 (m, 3H), 6.53 (s, 1H), 2.76 (q, J = 7.6 Hz, 2H), 1.38 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 161.3, 160.3, 134.3, 131.8, 128.9, 127.3, 101.7, 28.4, 10.0.

*2-Butyl-4-phenyl-6H-1,3-oxazin-6-one (**2o**).* white solid (25.1 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (m, 2H), 7.63−7.38 (m, 3H), 6.52 (s, 1H), 2.83−2.60 (t, J = 7.6 Hz, 2H), 1.83 (m, 2H), 1.46 (m, 2H), 0.98 (t, J = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 161.3, 160.3, 134.2, 131.8, 128.9, 127.2, 101.7, 34.7, 27.9, 22.1, 13.7. HRMS (ESI) calcd for $C_{14}H_{15}NO_2$ $[M + H]^+$: 230.1176. Found: 230.1176.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00965.

^{31}P NMR detection experiment of the reaction system and ^{1}H and ^{13}C NMR spectra of all products (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: aiwenlei@whu.edu.cn.

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Notes

The authors declare no competing financial interest.

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