JOC The Journal of Organic Chemistry

Article

Autoxidative C(sp2)-P Formation: Direct Phosphorylation of Heteroarenes under Oxygen, Metal-free and Solvent-free Conditions

Kai Luo, Yao-Zhong Chen, Li-Xian Chen, and Lei Wu

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b00592 • Publication Date (Web): 11 May 2016

Just Accepted

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

Autoxidative C(sp^2)-P Formation: Direct Phosphorylation of Heteroarenes under Oxygen, Metal-free and Solvent-free Conditions

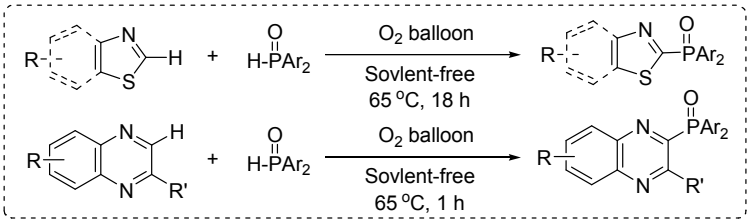
Kai Luo,[†,‡,§] Yao-Zhong Chen,[†,‡,§] Li-Xian Chen[†] AND Lei Wu[†,∫,*]

[†]*Jiangsu Key Laboratory of Pesticide Science and Department of Chemistry, College of Sciences, Nanjing Agricultural University, Nanjing 210095, China.*

[‡]*College of Plant Protection, Nanjing Agricultural University, Nanjing 210095, P. R. China.*

[∫]*Beijing National Laboratory for Molecular Sciences and Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.*

ABSTRACT: We reveal here a direct autoxidative phosphorylation of heteroarenes induced by oxygen under metal-free and solvent-free conditions. This new methodology provides an economical, operational simple and environmental friendly approach toward (Het)C(sp^2)-P formation with medium to excellent yields. Heteroarenes including thiazole and quinoxaline derivatives are applicable under standard condition, which is testified *via* a radical mechanism.



- **The first C(sp^2)-P formation by autoxidative coupling**
- **Sovent-free, Metal-free, Additive-free**
- **The first direct C-H phosphorylation of quinoxaline derivatives**

■ INTRODUCTION

The development of direct C-H bond functionalization facilitates the build of useful molecular architecture, which attracts high interest to academic and industrial chemists.[1] Many achievements have been made, but special activating, directing or leaving groups are indispensable for most of them. From the aspect of "green chemistry", oxidative coupling reactions between two C-H bonds would avoid unwanted waste and extra synthetic steps, along with hydrogen as "leaving group" and in the ideal case water as the only waste.[2] Cross dehydrogenative coupling (CDC) and autoxidative coupling reactions have emerged as a flourishing research area to generate C-C bonds. Leading scientists such as Li,[2a,3] Klussmann,[2c,4] Lei,[5] Jiao,[6]

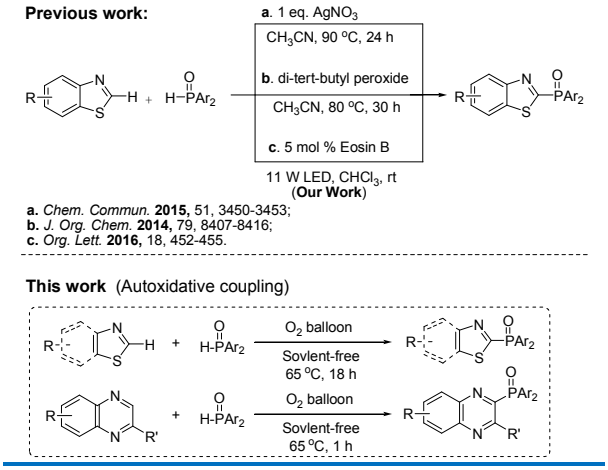
Jiang[7] and others [8] have contributed various carbon-carbon formations directly from two different C-H bonds under oxidative conditions, which have shown versatility and generality of these protocols. Generally, CDC reactions were mostly catalyzed by copper, iron, or palladium salts in combination with stoichiometric amount of synthetic oxidants including TBHP, TEMPO, DDQ *etc*.[2a] Nevertheless, autoxidative couplings presented a more environmental benign strategy using only molecular oxygen without metal catalysts.[2c] In terms of these criteria, several achievements have been extended to construct C-X (X = N, O, S *etc*) bonds as well,[9] intriguingly, C-N bond cleavage was also revealed under the autoxidation process.[10] However, to be noted, C(sp^2)-P formation as a hot research area has not been realized by autoxidative couplings.[11]

It's well-known that organophosphorus compounds play key roles in catalysis, organic synthesis, biochemistry and materials chemistry,[12] where phosphorus substituents regulate important biological, medicinal and material functions, and perform as ligands or directing group for transition metal catalysis. As such, the introduction of organophosphorus functionalities in convenient means continues to motivate methods for their synthesis. Of these methods, the transition metals catalyzed/ mediated coupling of phosphonate esters or phosphine oxides with electrophiles has been widely recognized as an efficient and promising approach for C(sp^2)-P bond formation. The phosphorylation of alkynes,[13] propargylic derivatives,[14] styrenes,[15] arylboronic acids,[16] aryl(pseudo) halides,[17] and (hetero)arenes[11] were extensively enabled by palladium, nickel, copper, rhodium and silver etc. Among which, the direct C-H functionalization of benzothiazoles with diarylphosphine oxides are extremely rare. One was reported by Zhang *et al.*, they demonstrated a silver nitrate-mediated phosphorylation of benzothiazoles and thiazoles in refluxing acetonitrile (Scheme 1, a).[11h] Chen *et al.* revealed another oxidative coupling of benzothiazoles and diarylphosphine oxides by heating with di-*tert*-butyl peroxide (DTBP) in acetonitrile at 80 ^{o}C (Scheme 1, b).[18] It's worthy to mention that these transformations and the aforementioned transition metals catalyzed C(sp^2)-P formations are associated with one or more limitations such as expensive, toxic or stoichiometric transition metals, air-sensitive ligands, synthetic oxidants, elevated temperatures. Thus, the potential development of such a synthesis with economical, operational simple and environmental friendly approach is highly demanded.

Recently, our group developed a novel cross-coupling hydrogen evolution of thiazoles derivatives with diarylphosphine oxides by organic dyes-sensitized photoredox catalysis without metal, oxidant or additive (Scheme 1, c).[19] In sharp contrast with traditional oxidative couplings, this photoredox catalytic reaction proceed worse under air or oxygen atmosphere, however, controlling experiments showed that a certain amount of target adduct formed under molecular oxygen without photocatalyst. This preliminary result spurs a potential C(sp^2)-P formations by autoxidative coupling. In continuing research on synthesis and application

of organophosphorous chemistry, [20] herein we report, for the first time, the autoxidative coupling of heteroarenes (thiazole and quinoxaline derivatives) with diarylphosphine oxides under oxygen, metal-free and solvent-free conditions (Scheme 1, d).

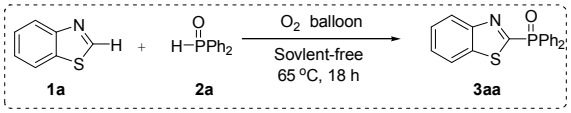
Scheme 1. Previous direct C-H functionalization of benzothiazoles with diarylphosphine oxides and this work.



■ RESULTS AND DISCUSSION

The Table 1 depicts the optimized conditions after systematic screening, where the parameters alter in solvent, temperature, atmosphere and reaction time. Initially, as the aforementioned result, 9% isolated yield of 2-(diphenylphosphine oxide)benzo[d]thiazole (**3aa**) was detected in the coupling of benzothiazole (**1a**) with diphenylphosphine oxide (**2a**) in refluxing chloroform under oxygen atmosphere (entry 1). A series of solvents including 1,2-dichloroethane, THF, dioxane, DMF, DME, EtOH, and toluene were then screened to improve the yields. However, the couplings in common organic solvents only afforded low yields, albeit 21% yield of adduct were isolated in 1,1-dichloroethane (entry 2). Quite interestingly, the couplings under solvent-free conditions dramatically improved the yield to 97% when heated to 65 °C (entry 11). Higher reaction temperature of 100 °C led to lower yield (entry 13), which might be contributed to the decomposition of substrates. Notably, the oxygen content significantly affected the coupling; only 37% of product **3aa** was detected under solvent-free and air with heating (entry 14), and the substrates remained intact under the oxygen-free condition (entry 18). Moreover, the ratios of substrates impacted the results as well. The excess of diphenylphosphine oxide (**2a**) is necessary to obtain satisfactory yields. These results indicate that oxygen atmosphere, solvent-free, appropriate temperature and substrate ratios are essential to achieve the reaction efficiently.

Table 1. Reaction condition optimizations: autoxidative coupling of benzothiazoles and diphenylphosphine oxides.[a]



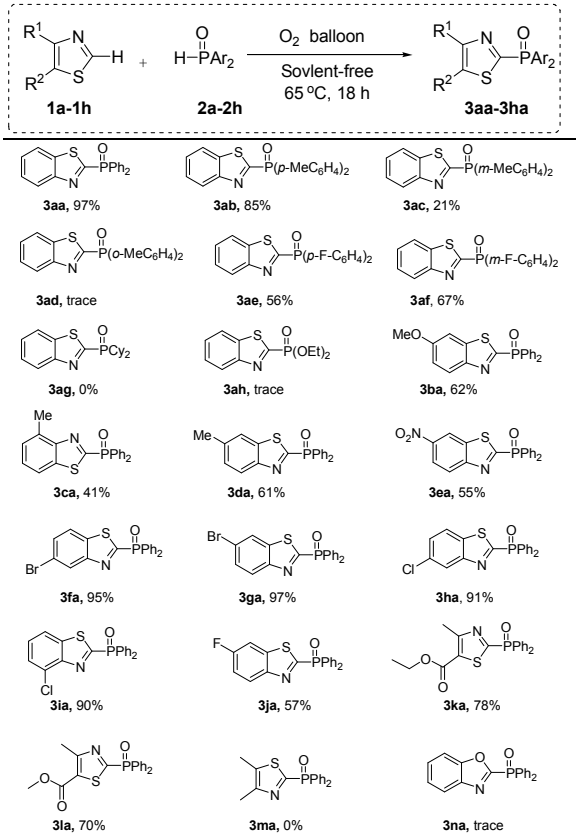
entry	variations (based on standard conditions)	yield of **3aa**[b]
1	$CHCl_3$, reflux, 24 h	9
2	1,2-dichloroethane, 65 °C, 24 h	21
3	THF, reflux, 24 h	trace
4	dioxane, , 65 °C, 24 h	trace
5	DMF, 65 °C, 24 h	N.R.
6	DME, 65 °C, 24 h	17
7	EtOH, 65 °C, 24 h	trace
8	toluene, 65 °C, 24 h	trace
9	20°C	33
10	50°C	91
11	**None**	**97**
12	80°C	85
13	100°C	52
14	air	37
15	N_2	0
16	**1a**:**2a**=1:1	69
17[c]	**1a**:**2a**=3:1	37
18[d]	None	97

[a]0.2 mmol benzothiazole, 1 mmol diphenylphosphine oxide, oxygen balloon, 65 °C, 18 h; [b]Isolated yield based on benzothiazole(**1a**). [c]Isolated yield based on diphenylphosphine oxide (**2a**).[d]In dark under standard conditions.

On the basis of this optimized conditions, we further evaluated the scope of thiazole derivatives and diarylphosphine oxides that could participate in the autoxidative coupling. In general, the reactions were remarkably sensitive to the electronic properties of substitutions on thiazole derivatives and phosphine oxides. As shown in Scheme 2, diarylphosphine oxides bearing electron-donating or withdrawing groups at their *para*- and *meta*-positions, including methoxy, and methyl, were applicable to the coupling with yields up to 85% (compounds **3ab**, **3ac**, **3ae**, **3af**). Methyl substitutions on *ortho*-positions of phosphine oxide moieties led to the failure of coupling due to steric hindrance (compound **3ad**). This effect was found to be extremely detrimental for di(2,4,6-trimethylphenyl)phosphine oxide, the coupling ceased to afford couple of decompositions. In addition, dialkylphosphine oxides and dialkylphosphites (**3ag**, **3ah**) exhibited no reactivity according to the standard conditions. Arylthiazoles with electron-withdrawing groups, such as Br- and Cl-, were coupled with diarylphosphine oxides to afford the corresponding adducts in excellent yields

(**3fa**-**3ia**). Substrates with strong electron-donating methoxy (**3ba**) and strong electron-withdrawing nitro groups (**3ea**) gave comparable lower yields, which might be ascribed to the relatively unstable radical intermediates. Notably, ethyl 4-methyl thiazole-5-carboxylate and methyl 4-methyl thiazole-5-carboxylate could also react under the standard conditions affording the products **3ka**, **3la**, in yields of 78% and 70%, respectively. Unfortunately, 4,5-dimethylthiazole (**3ma**) was left intact even after systematic screening, in part because of the less of conjugation on substrates to stabilize the radical intermediate. An attempt to couple benzoxazole with diphenylphosphine oxide under standard conditions was found to be sluggish as well.

Scheme 2. Autoxidative coupling of thiazole derivatives and diarylphosphine oxides.[a,b]

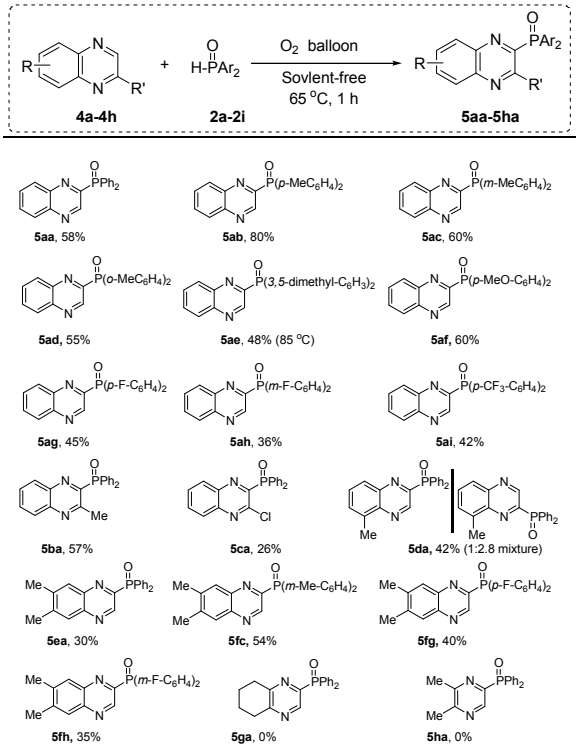


[a] 0.2 mmol thiazole derivatives, 1 mmol diarylphosphine oxide, oxygen balloon, 65 °C, 18 h; [b]Isolated yield based on thiazole derivatives.

Further efforts were devoted to apply this autoxidative coupling to other heterocycles. Benzothiophene, benzofuran, indole, quinoline and quinazoline derivatives were investigated with diarylphosphine oxides affording negative results, where quinoline and quinazoline derivatives formed C(sp^3)-P bonds leading to reductive addition products (see details in experimental section).[21] To be noted, quinoxalines exhibited similar reactivity to benzothiazoles while subjected to the above conditions. It's well known that phosphinyl functionalized quinoxaline are versatile intermediates in medicinal chemistry, coordination chemistry and catalysis. However, the syntheses of diarylphosphinyl quinoxalines are rather trivial and limited.[22] For an elegant example, in 2015, Han *et al.* disclosed a nickel catalyzed C-O/P(O)-H coupling of quinoxalin-3-yl pivalate with diphenylphosphine oxide to access the 2-(diphenylphosphino) quinoxaline with 42% yield.[22c] To the best of our knowledge, the direct C-H phosphorylation of quinoxaline derivatives has not been established yet.

The optimized conditions for thiazole derivatives were applied here directly (oxygen balloon, 65 ^{o}C, solvent-free), with a ratio of 1.1:1 for quinoxaline (**4a-h**) and diarylphosphine oxides (**2a-i**). Quite interestingly, while the mixtures solidified within 1 h, the coupling of diphenylphosphine oxide (**2a**) with quinoxaline (**4a**) underwent completely to afford the adduct **5aa** with 58% yield. Subsequently, varieties of diarylphosphine oxides and quinoxaline derivatives were allowed to react. As shown in **Scheme 3**, all kinds of diarylphosphine oxides bearing electron-donating and withdrawing groups gave medium to good yields (**5ab**-**5ai**), where electron-withdrawing groups slightly impaired the reaction. Substituents on quinoxaline moiety also proceeded with acceptable yields. When 5-methyl-quinoxaline (**4d**) was used, the coupling reaction run smoothly to produce **5da** in 42% combined yield with a ratio of 1:2.8. In regard to the 5,6,7,8-tetrahydroquinoxaline and 2,3-dimethylpyrazine, no reactions were observed, which further indicated the larger conjugation on heteroarenes is crucial to enable the autoxidative coupling.

Scheme 3. Autoxidative coupling of quinoxaline derivatives and diarylphosphine oxides.[a,b]

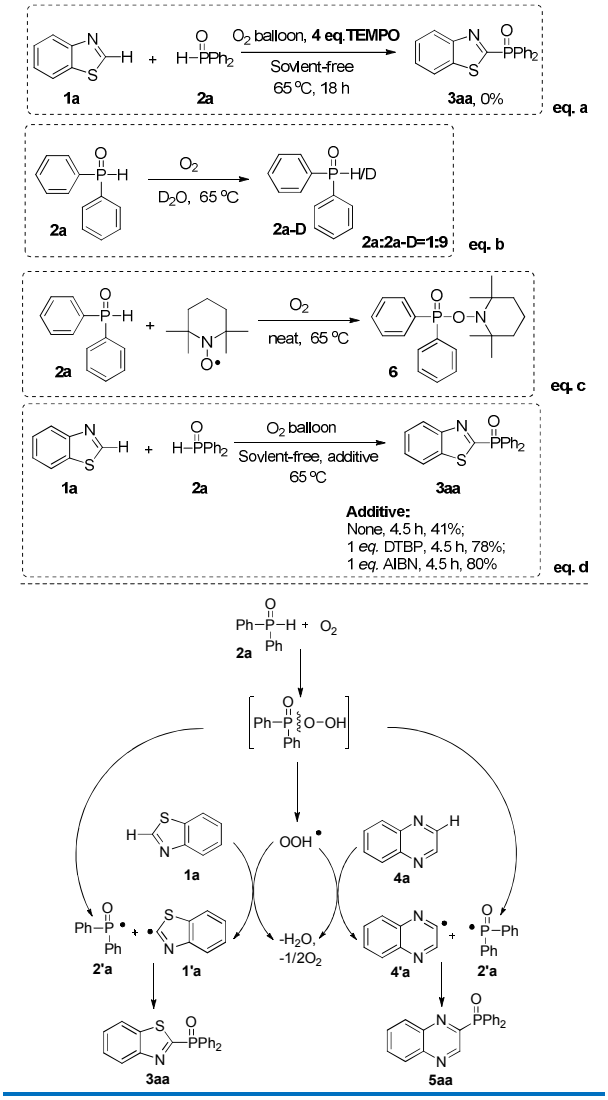


[a]0.22 mmol quinoxaline derivatives, 0.2 mmol diarylphosphine oxide, oxygen balloon, 65 °C, 1 h; [b]Isolated yield based on diarylphosphine oxide.

In order to gain an understanding of the reaction mechanisms of this C(sp^2)-P formation, we performed some controlling and deuterium experiments. Initially, 4 equivalents of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was found to suppress the reaction completely, thus, a radical mechanism might occur in the process (**Scheme 4,** eq. a). The isolation of deuterium exchange product 2a-D and TEMPO captured adduct **6** testified the initiation of coupling from P-radical (eq. b and c, see details in supporting information). Next, a rapid color change of $FeCl_2$/KSCN solution toward reaction mixtures indicated the generation of peroxide from diphenylphosphine oxide. Finally, the utility of common radical initiators, AIBN and di-*tert*-butyl peroxide (DTBP), dramatically accelerated the coupling reactions while combining with molecular oxygen under solvent-free conditions, which further confirmed the radical mechanism of this reaction (eq. d). The above results coupled with previous reports on oxidative couplings,[2c,18] collectively point to a proposed mechanism in Scheme 4. The oxygen excite the diphenylphosphine oxide under heat to generate a P-radical **2'a**, along with a peroxide radical. The peroxide radical undergoes hydrogen atom abstraction of the 2-position of C(sp^2)-H of benzothiazole to form intermediate **1'a**, with H_2O and oxygen released as well.

Eventually, two radicals **1'a** and **2'a** combine to give the coupling product **3aa**.

Scheme 4. Tentative mechanism for the autoxidative coupling of heteroarenes with diphenylphosphine oxide.



■ CONCLUSIONS

In conclusion, a direct autoxidative phosphorylation of heteroarenes induced by oxygen under metal-free and solvent-free conditions was disclosed. Thiazole and quinoxaline derivatives were enabled to coupling with various diarylphosphine oxides by this novel economical, operational simple and environmental friendly approach toward (Het)C(sp^2)-P formation. Mechanistic studies verified this coupling undergoes

through a radical pathway initiated by diarylphosphine oxide.

■ EXPERIMENTAL SECTION

General Methods. Solvents and reagents were reagent grade and used without purification unless otherwise noted. Anhydrous solvents were obtained as follows: THF, 1,4-dioxane and toluene were dried by distillation from sodium and benzophenone; $CHCl_3$, DMF were redistilled over CaH_2. All reactions were carried out in oven dried glassware under oxygen unless otherwise specified. Column chromatography was performed using silica gel (300-400 mesh). ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded in $CDCl_3$ operating at 400, 100 and 162 MHz in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm (δ). Coupling constants are reported in Hertz (Hz). Spectral splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad.

Synthetic Procedures. *General Procedure for the Autoxidative coupling of thiazole derivatives with diarylphosphine oxides to Access compounds (**3**): 2-(diphenylphosphine oxide)benzo[d]thiazole (**3aa**)*[19]. To a 5 mL vial equipped with oxygen balloon was added benzo[d]thiazole (**1a**, 27.0 mg, 0.2 mmol) and diphenylphosphine oxide (**2a**, 202.1 mg, 1 mmol). The reaction was then heated to 65 ^{0}C for 18 hours until the complete consuming of starting materials monitored by TLC. After being cooling down, the mixtures were quenched by adding water, and then extracted with ethyl acetate (3 mL×2). The crude product was purified on flash chromatography, with ethyl acetate/petroleum ether (1:1) as eluents to afford product **3aa** as white solid (67 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.8 Hz, 1H), 8.05-8.01 (m, 1H), 8.01-7.93 (m, 4H), 7.65-7.43 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6 (d, J = 127.0 Hz), 155.2 (d, J = 21.6 Hz), 136.6, 132.5 (d, J = 2.9 Hz), 131.8 (d, J = 10.2 Hz), 130.8 (d, J = 109.0 Hz), 128.5 (d, J = 12.8 Hz), 126.5 (d, J = 4.3 Hz), 124.6, 121.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.07 (s).

*benzo[d]thiazol-2-yldi-p-tolylphosphine oxide(**3ab**)*.[19] A yellow liquid (60 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.84 (dd, J = 12.5, 8.1 Hz, 4H), 7.49 (tdd, J = 15.1, 10.8, 4.2 Hz, 2H), 7.29 (dd, J = 8.1, 2.8 Hz, 4H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2 (d, J = 126.3 Hz), 155.2 (d, J = 21.4 Hz), 143.1 (d, J = 2.9 Hz), 136.6, 131.8 (d, J = 10.6 Hz), 129.2 (d, J = 13.2 Hz), 127.6 (d, J = 111.6 Hz), 126.4 (d, J = 6.6 Hz), 124.5, 121.9, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.80 (s).

*benzo[d]thiazol-2-yldi-m-tolylphosphine oxide(**3ac**)*.[19] A white solid (15 mg, 21% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 7.8 Hz, 1H), 7.76 (m, 4H), 7.53 (m, 2H), 7.44-7.31 (m, 4H), 2.39 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0 (d, J = 126.0 Hz), 155.3 (d, J = 21.4 Hz), 138.5 (d, J

= 12.7 Hz), 136.8, 133.4 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 10.0 Hz), 130.6 (d, *J* = 108.5 Hz), 129.0 (d, *J* = 10.5 Hz), 128.5 (d, *J* = 13.6 Hz), 126.5 (d, *J* = 6.3 Hz), 124.7, 122.0, 21.4 . ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.75 (s).

*benzo[d]thiazol-2-ylbis(4-fluorophenyl)phosphine oxide(**3ae**).*[19] A white solid (44 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.1 Hz, 1H), 8.03-7.96 (m, 5H), 7.52 (dt, *J* = 15.0, 7.2 Hz, 2H), 7.20 (td, *J* = 8.6, 1.9 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9-166.0 (m), 165.4 (s), 164.1 (d, *J* = 3.4 Hz), 155.1 (d, *J* = 21.9 Hz), 136.5, 134.3 (dd, *J* = 11.7, 9.1 Hz), 126.7 (dd, *J* = 113.1, 3.0 Hz), 126.7, 124.5, 122.0, 116.0 (dd, *J* = 21.6, 14.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.29 (s).

*benzo[d]thiazol-2-ylbis(3-fluorophenyl)phosphine oxide(**3af**).*[19] A white solid (50 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.86-7.66 (m, 4H), 7.63-7.39 (m, 4H), 7.35-7.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0 (d, *J* = 131.3 Hz), 163.6 (d, *J* = 18.2 Hz), 161.1 (d, *J* = 18.2 Hz), 155.1 (d, *J* = 22.2 Hz), 136.6 (s), 133.0 (dd, *J* = 108.8, 5.9 Hz), 130.7 (dd, *J* = 15.0, 7.4 Hz), 127.5 (dd, *J* = 9.5, 3.3 Hz), 126.9 (d, *J* = 3.1 Hz), 124.8, 122.05, 120.0 (dd, *J* = 21.2, 2.6 Hz), 118.6 (dd, *J* = 22.9, 11.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.78 (t, *J* = 6.3 Hz).

*(6-methoxybenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3ba**).*[19] A yellow liquid (49 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 9.1 Hz, 1H), 8.00-7.91 (m, 4H), 7.57 (td, *J* = 7.3, 1.4 Hz, 2H), 7.53-7.45 (m, 4H), 7.41 (d, *J* = 2.4 Hz, 1H), 7.15 (dd, *J* = 9.1, 2.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2 (d, *J* = 130.0 Hz), 158.8, 150.0 (d, *J* = 22.0 Hz), 138.5, 132.5 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 10.2 Hz), 131.1 (d, *J* = 109.0 Hz), 128.5 (d, *J* = 12.8 Hz), 125.2, 117.1, 103.3, 55.8. ^{31}P NMR (122 MHz, $CDCl_3$) δ 20.07 (s).

*(4-methylbenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3ca**).*[19] A white solid (29 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.94 (m, 4H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.56 (dd, *J* = 10.4, 4.3 Hz, 2H), 7.49 (td, *J* = 7.4, 3.2 Hz, 4H), 7.36 (dt, *J* = 14.8, 7.3 Hz, 2H), 2.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7 (d, *J* = 129.0 Hz), 154.8 (d, *J* = 21.1 Hz), 136.5, 134.7, 132.4 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 10.1 Hz), 130.6, 128.4 (d, *J* = 12.8 Hz), 126.9, 126.5, 119.3, 18.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.39 (s).

*(6-methylbenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3da**).*[19] A white solid (43 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.95 (dd, *J* = 12.6, 7.2 Hz, 4H), 7.78 (s, 1H), 7.60 – 7.52 (m, 2H), 7.48 (td, *J* = 7.4, 3.0 Hz, 4H), 7.35 (d, *J* = 8.4 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1 (d, *J* = 128.4 Hz), 153.5 (d, *J* = 21.9 Hz), 137.0 (d, *J* = 5.4 Hz), 132.5 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 10.2 Hz), 131.0 (d, *J* = 109.0 Hz), 128.6 (d, *J* = 12.8 Hz), 128.4, 124.1, 121.5, 21.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.12 (s).

*(6-nitrobenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3ea**)*.[19] A yellow solid (43 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (d, *J* = 2.2 Hz, 1H), 8.42 (dd, *J* = 9.1, 2.2 Hz, 1H), 8.30 (d, *J* = 9.1 Hz, 1H), 8.09-7.88 (m, 4H), 7.63 (td, *J* = 7.3, 1.4 Hz, 2H), 7.59-7.48 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2 (d, *J* = 119.5 Hz), 158.4 (d, *J* = 20.8 Hz), 145.8, 137.0, 133.0 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 10.3 Hz), 130.0 (d, *J* = 109.5 Hz), 128.8 (d, *J* = 13.0 Hz), 125.2, 121.9, 118.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.90 (s).

*(5-bromobenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3fa**)*.[19] A white solid (92 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 1.1 Hz, 1H), 7.97 (dd, *J* = 12.6, 7.4 Hz, 4H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 3H), 7.50 (td, *J* = 7.4, 3.1 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0 (d, *J* = 124.2 Hz), 156.4 (d, *J* = 21.4 Hz), 135.5, 132.7 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 10.2 Hz), 130.6 (d, *J* = 109.1 Hz), 129.8, 128.7 (d, *J* = 12.9 Hz), 127.4, 123.1, 120.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.77 (s).

*(6-bromobenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3ga**)*.[19] A white solid (80 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.96 (dd, *J* = 12.6, 7.6 Hz, 4H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.51 (dt, *J* = 7.0, 3.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5 (d, *J* = 125.1 Hz), 154.1 (d, *J* = 21.4 Hz), 138.3, 132.7 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 10.3 Hz), 130.5 (d, J = 109.1 Hz), 130.3, 128.6 (d, *J* = 12.9 Hz), 125.7, 124.5, 120.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.97 (s).

*(5-chlorobenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3ha**)*.[19] A white solid (68 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.9 Hz, 1H), 8.02-7.93 (m, 4H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.63-7.55 (m, 2H), 7.51 (tdd, *J* = 8.2, 3.2, 1.2 Hz, 4H), 7.45 (dd, *J* = 8.6, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1 (d, *J* = 124.3 Hz), 156.0 (d, *J* = 21.5 Hz), 135.0, 132.8, 132.7 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 10.3 Hz), 130.6 (d, *J* = 109.2 Hz), 128.7 (d, *J* = 12.9 Hz), 127.2, 124.3, 122.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.86 (s).

*(4-chlorobenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3ia**)*.[19] A white solid (66 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.02 (m, 4H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.56 (m, 1H), 7.54 – 7.47 (m, 6H), 7.37 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (100MHz, $CDCl_3$) δ 167.8 (d, *J* = 124.7 Hz), 152.3 (d, *J* = 21.5 Hz), 138.1, 132.6 (d, *J* = 2.9 Hz), 131.8(d, *J* = 10.2 Hz), 131.2, 130.1, 129.5, 128.6 (d, J = 12.9 Hz), 126.9 (d, J = 24.1 Hz), 120.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.00 (s).

*(6-fluorobenzo[d]thiazol-2-yl)diphenylphosphine oxide(**3ja**)*.[19] A white solid (40 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 9.0, 4.8 Hz, 1H), 7.96 (dd, *J* = 12.6, 7.3 Hz, 4H), 7.66 (dd, *J* = 8.0, 2.3 Hz, 1H), 7.59-7.55 (m, 2H), 7.49 (td, *J* = 7.4, 3.1 Hz, 4H), 7.30-7.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 (dd, *J* = 126.5, 3.6 Hz), 161.1 (d, *J* = 249.0 Hz),151.9 (d, *J* = 21.8 Hz), 137.8 (d, *J* = 11.4 Hz), 132.6 (d, *J* = 2.9 Hz), 131.7 (d, *J* = 10.3 Hz), 130.6 (d, *J* = 109.2 Hz), 128.6 (d, *J* = 12.9 Hz), 125.7 (d, *J* = 9.7 Hz), 115.8 (d, *J* = 25.3 Hz), 107.9 (d, *J* = 26.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.91 (s).

*ethyl 2-(diphenylphosphoryl)-4-methylthiazole-5-carboxylate(**3ka**)*.[19] A white solid (59 mg, 78% yield). ^{1}H

NMR (400 MHz, $CDCl_3$) δ 7.97-7.86 (m, 4H), 7.65-7.56 (m, 2H), 7.51 (tdd, *J* = 8.2, 3.2, 1.2 Hz, 4H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.82 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6 (d, *J* = 125.8 Hz), 163.0 (d, *J* = 19.0 Hz), 161.6, 132.6 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 10.3 Hz), 130.8 (d, *J* = 109.4 Hz), 128.6 (d, *J* = 12.8 Hz), 127.4, 61.7, 17.6, 14.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.80 (s).

*methyl 2-(diphenylphosphoryl)-4-methylthiazole-5-carboxylate(**3la**).*[19] A white solid (48 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.90 (m, 4H), 7.63-7.58 (m, 2H), 7.55-7.50 (m, 4H), 3.91 (s, 3H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8 (d, *J* = 125.6 Hz), 163.2 (d, *J* = 19.0 Hz), 162.1, 132.7 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 10.3 Hz), 130.7 (d, *J* = 109.5 Hz), 128.7 (d, *J* = 12.9 Hz), 126.9, 52.5, 17.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.78 (s).

*General Procedure for the Autoxidative coupling of quinoxaline derivatives with diarylphosphine oxides to Access compounds (**5**): diphenyl(quinoxalin-2-yl)phosphine oxide(**5aa**).*[22c] To a 5 mL vial equipped with oxygen balloon was added quinoxaline (**4a**, 28.6 mg, 0.22 mmol) and diphenylphosphine oxide (**2a**, 40.4 mg, 0.2 mmol). The reaction was then heated to 65 ^{0}C for 1 hour until the complete consuming of starting materials monitored by TLC. After being cooling down, the mixtures were quenched by adding water, and then extracted with ethyl acetate (3 mL×2). The crude product was purified on flash chromatography, with ethyl acetate/petroleum ether (1:1) as eluents to afford product **5aa** as yellow solids (38 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.18-8.14 (m, 2H), 7.99-7.94 (m, 4H), 7.86-7.81 (m, 2H), 7.56-7.53 (m, 2H), 7.48 (tdd, *J* = 8.3, 3.1, 1.3 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, *J* = 124.2 Hz), 146.5 (d, *J* = 22.1 Hz), 142.7 (d, *J* = 2.3 Hz), 142.2 (d, *J* = 17.1 Hz), 132.3 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 9.6 Hz), 131.9 , 131.5 (d, J = 104.2 Hz), 130.7, 130.20, 129.7 (d, *J* = 1.8 Hz), 128.6 (d, *J* = 12.3 Hz). ^{31}P NMR (162 MHz, CDCl3) δ 20.40 (s).

*quinoxalin-2-yldi-p-tolylphosphine oxide(**5ab**).* A brown solid, m.p.: 178.7-180.1 ^{o}C (85 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.15 (dd, *J* = 11.0, 4.2 Hz, 2H), 7.86-7.79 (m, 6H), 7.29 (dd, *J* = 8.1, 2.6 Hz, 4H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6 (d, *J* = 123.9 Hz), 146.3 (d, *J* = 22.1 Hz), 142.8 (d, *J* = 2.8 Hz), 142.5 (d, *J* = 2.3 Hz), 142.1 (d, *J* = 16.9 Hz), 132.1 (d, *J* = 10.0 Hz), 131.1 (d, *J* = 120.9 Hz), 130.1, 129.5, 129.2 (d, *J* = 12.8 Hz), 128.1 (d, *J* = 107.4 Hz), 21.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.33 (s). HR-MS m/z (ESI): $C_{22}H_{20}N_2OP$ (calcd.: 359.1313), found: 359.1307 ($[M+H]^+$). IR (film) *v* 3031, 2907, 2856, 1599, 1485, 1360, 1321, 1216, 1192, 1116, 1091, 1017, 967, 812, 769.

*quinoxalin-2-yldi-m-tolylphosphine oxide(**5ac**).* A yellow solid, m.p.: 143.8-144.4 ^{o}C (63 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.17 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.88-7.78 (m, 4H), 7.73 (dd, *J* = 12.7, 4.9 Hz, 2H), 7.39-7.36 (m, 4H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3 (d, *J* = 123.6 Hz), 146.3 (d, *J* = 22.1 Hz), 142.5 (d, *J* = 2.3 Hz), 142.1 (d, *J* = 17.1 Hz), 138.4 (d, *J* = 12.2 Hz), 133.0 (d, *J* = 2.9

Hz), 132.3 (d, *J* = 9.4 Hz), 131.8, 131.6, 130.6, 129.8 (dd, *J* = 62.3, 1.4 Hz), 129.1 (d, *J* = 9.8 Hz), 128.3 (d, *J* = 13.1 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.98 (s). HR-MS m/z (ESI): $C_{22}H_{19}N_2OPNa$ (calcd.: 381.1133), found: 381.1125 ($[M+Na]^+$). IR (film) *v* 3030, 2947, 2847, 1659, 1499, 1404, 1320, 1217, 1173, 1120, 1060, 1027, 872, 766, 668.

*quinoxalin-2-yldi-o-tolylphosphine oxide(**5ad**).* A yellow solid, m.p.: 146.2-147.5 °C (45 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.22 (d, J = 7.6 Hz, 1H), 8.12 (d, J = 7.8 Hz, 1H), 7.93 – 7.88 (m, 1H), 7.86-7.82 (m, 1H), 7.46 (td, *J* = 14.5, 7.6 Hz, 4H), 7.33 (dd, *J* = 7.4, 4.6 Hz, 2H), 7.23 (t, *J* = 6.6 Hz, 2H), 2.50 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (d, *J* = 122.9 Hz), 147.2 (d, *J* = 22.6 Hz), 143.1 (d, *J* = 8.5 Hz), 142.5, 142.0 (d, *J* = 16.9 Hz), 133.1 (d, *J* = 12.1 Hz), 132.4, 132.2-131.6 (m), 130.5 (d, *J* = 34.5 Hz), 129.6 (d, *J* = 102.5 Hz), 129.6, 125.6 (d, *J* = 12.9 Hz), 21.9.^{31}P NMR (162 MHz, $CDCl_3$) δ 29.77 (s). HR-MS m/z (ESI): $C_{22}H_{20}N_2OP$ (calcd.:359.1313)，found: 359.1301（$[M+H]^+$）. IR (film) *v* 3055, 2982, 2923, 1585, 1561, 1473, 1448, 1361, 1273, 1183, 1134, 1068, 966, 869, 754.

*bis(3,5-dimethylphenyl)(quinoxalin-2-yl)phosphine oxide(**5ae**).* A yellow red solid, m.p.: 144.6-146.3 °C (56 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.19 (dd, *J* = 6.1, 1.9 Hz, 2H), 7.90-7.82 (m, 2H), 7.55 (d, *J* = 12.4 Hz, 4H), 7.19 (s, 2H), 2.35 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (d, J = 123.0 Hz), 146.5 (d, *J* = 22.1 Hz), 142.6 (d, *J* = 2.3 Hz), 142.3 (d, *J* = 17.0 Hz), 138.3 (d, *J* = 13.0 Hz), 134.1 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 120.6 Hz), 131.1 (d, *J* = 103.3 Hz), 130.3, 129.7, 129.6, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.87 (s). HR-MS m/z (ESI): $C_{24}H_{24}N_2OP$ (calcd.: 387.1626), Found: 387.1620 ($[M+H]^+$). IR (film) *v* 3047, 2911, 2851, 1529, 1485, 1441, 1362, 1317, 1265, 1190, 1130, 1099, 1033, 966, 848, 769.

*bis(4-methoxyphenyl)(quinoxalin-2-yl)phosphine oxide(**5af**).* A white solid, m.p.:182.5-184.1 °C (67 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.16-8.12 (m, 2H), 7.87-7.79 (m, 6H), 6.97 (dd, J = 8.8, 2.2 Hz, 4H), 3.81 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, *J* = 2.9 Hz), 152.9 (d, *J* = 124.8 Hz), 146.4 (d, *J* = 22.1 Hz), 142.5 (d, *J* = 2.3 Hz), 142.2 (d, *J* = 17.0 Hz), 134.1 (d, *J* = 11.0 Hz), 131.8, 130.6, 129.9 (d, *J* = 57.9 Hz), 122.7 (d, *J* = 112.0 Hz), 114.2 (d, *J* = 13.4 Hz), 55.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.32 (s). HR-MS m/z (ESI): $C_{22}H_{19}N_2O_3PNa$ (calcd.: 413.1031), found: 413.1024 ($[M+Na]^+$). IR (film) *v* 3100, 2978, 2852, 1597, 1505, 1405, 1259, 1177, 1121, 1059, 1024, 965, 869, 765.

*bis(4-fluorophenyl)(quinoxalin-2-yl)phosphine oxide(**5ag**).* A yellow solid, m.p.: 178.3-179.5 °C (50 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.19 (dd, *J* = 17.0, 7.8 Hz, 2H), 7.99 (ddd, *J* = 11.7, 8.5, 5.6 Hz, 4H), 7.93-7.87 (m, 2H), 7.21 (td, *J* = 8.7, 2.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4 (d, *J* = 257.8 Hz), 151.7 (d, *J* = 126.5 Hz), 146.3 (d, *J* = 22.2 Hz), 142.8, 142.1 (d, *J* = 17.4 Hz), 134.7 (dd, *J* = 11.0, 9.0 Hz), 131.6 (d, *J* = 124.7 Hz), 129.9 (d, *J* = 31.3 Hz), 127.3 (d, *J* = 108.4 Hz), 116.1 (dd, *J* = 21.5, 13.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.86 (s). HR-MS m/z (ESI): $C_{20}H_{14}F_2N_2OP$ (calcd.: 367.0812),

found: 367.0806 ([M+H]$^+$). IR (film) *v* 3067, 2911, 2843, 1584, 1500, 1486, 1397, 1361, 1320, 1234, 1194, 1116, 1090, 963, 815, 760.

*bis(3-fluorophenyl)(quinoxalin-2-yl)phosphine oxide(**5ah**).* An orange solid, m.p.: 143.6-144.7 ^{o}C (37 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.20 (d, *J* = 8.2 Hz, 2H), 7.89 (dq, *J* = 7.0, 5.6 Hz, 2H), 7.79 (dd, *J* = 11.7, 7.7 Hz, 2H), 7.74-7.68 (m, 2H), 7.53-7.47 (m, 2H), 7.29-7.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7 (d, *J* = 17.5 Hz), 161.2 (d, *J* = 17.5 Hz), 151.0 (d, *J* = 127.2 Hz), 146.3 (d, *J* = 22.4 Hz), 142.9, 142.1 (d, *J* = 17.5 Hz), 134.2 (d, *J* = 5.8 Hz), 133.1 (d, *J* = 5.8 Hz), 131.7 (d, *J* = 129.7 Hz), 130.7 (dd, *J* = 14.4, 7.5 Hz), 130.2-129.7 (m), 127.8 (dd, *J* = 8.9, 3.3 Hz), 119.8 (dd, *J* = 21.2, 2.6 Hz), 118.9 (dd, *J* = 22.8, 10.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.09 (t, *J* = 6.2 Hz). HR-MS m/z (ESI): $C_{20}H_{13}F_2N_2OPNa$ (calcd.: 389.0631), found: 389.0622 ([M+Na]$^+$). IR (film) *v* 3047, 2919, 2843, 1583, 1472, 1418, 1363, 1323, 1226, 1193, 1127, 1093, 966, 879, 764.

*quinoxalin-2-ylbis(4-(trifluoromethyl)phenyl)phosphine oxide(**5ai**).* A yellow solid, m.p.: 136.8-138.3 ^{o}C (41 mg, 42% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.19 (td, *J* = 12.1, 8.5 Hz, 6H), 7.92 (dt, *J* = 15.0, 6.2 Hz, 2H), 7.78 (d, *J* = 6.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5 (d, *J* = 127.4 Hz), 146.3 (d, *J* = 22.4 Hz), 143.0 (d, *J* = 2.3 Hz), 142.1 (d, *J* = 17.5 Hz), 135.3 (d, *J* = 103.0 Hz), 134.3 (dd, *J* = 32.9, 3.0 Hz), 132.5 (d, *J* = 9.7 Hz), 131.3, 130.1, 129.9 (d, *J* = 1.9 Hz), 125.7-125.5 (m), 123.4 (d, *J* = 273.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.79. HR-MS m/z (ESI): $C_{22}H_{14}F_6N_2OP$ (calcd.: 467.0748), found: 467.0740 ([M+H]$^+$). IR (film) *v* 3019, 2939, 2835, 1587, 1502, 1397, 1363, 1321, 1217, 1192, 1117, 1101, 1062, 1023, 963, 865.

*(3-methylquinoxalin-2-yl)diphenylphosphine oxide(**5ba**).*[22a] A dark red solid. m.p.: 159.1-160.3 ^{o}C (58 mg, 57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.83 (dt, *J* = 14.8, 7.5 Hz, 5H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.50 (td, *J* = 7.7, 2.7 Hz, 4H), 3.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7 (d, *J* = 22.1 Hz), 151.5 (d, *J* = 124.2 Hz), 141.7, 139.9 (d, *J* = 17.5 Hz), 132.2 (d, *J* = 9.4 Hz), 132.0 (d, *J* = 15.4 Hz), 131.1, 130.0, 129.4, 128.5 (d, *J* = 2.2 Hz), 128.4 (d, *J* = 12.3 Hz), 23.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.28.

*(3-chloroquinoxalin-2-yl)diphenylphosphine oxide(**5ca**).* A yellow solid, m.p.: 198.8-199.5 ^{o}C (29 mg, 26% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz,1H), 7.97 (d, J = 8.4 Hz,1H), 7.90-7.75 (m, 6H), 7.60 (td, *J* = 7.3, 1.3 Hz,2H), 7.54-7.49 (m,4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (d, *J* = 127.1 Hz), 148.7 (d, *J* = 21.6 Hz), 141.8, 139.9 (d, *J* = 15.3 Hz), 133.2, 132.4 (d, *J* = 2.7 Hz), 132.1 (d, *J* = 9.7 Hz), 130.5 (d, *J* = 108.3 Hz), 130.4 (d, *J* = 54.3 Hz), 128.5 (d, *J* = 12.7 Hz), 128.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.61. HR-MS m/z (ESI): $C_{20}H_{14}ClN_2OPNa$ (calcd.: 387.0430), found: 387.0421 ([M+Na]$^+$). IR (film) *v* 3059, 2923, 2839, 1554, 1477, 1437, 1369, 1333, 1252, 1175, 1115, 1099, 1009, 772, 754, 725, 707, 694.

*(5-methylquinoxalin-2-yl)diphenylphosphine oxide(**5da-1**).* A brown solid, m.p.: 155.2-156.3 °C (23 mg, 11% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.00-7.98 (m, 2H), 7.96 (d, J = 1.4 Hz, 1H), 7.95 (s, 1H), 7.93 (d, *J* = 1.3 Hz, 1H), 7.70 (dd, *J* = 9.5, 4.7 Hz, 2H), 7.57-7.53 (m, 2H), 7.48 (ddd, *J* = 7.1, 5.4, 2.5 Hz, 4H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6 (d, *J* = 124.8 Hz), 145.2 (d, *J* = 22.3 Hz), 142.4 (d, *J* = 17.0 Hz), 141.9 (d, *J* = 2.3 Hz), 138.1, 132.2 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 9.6 Hz), 131.1 (d, *J* = 131.8 Hz), 131.1, 128.5 (d, *J* = 12.3 Hz), 128.0, 17.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.49. HR-MS m/z (ESI): $C_{21}H_{18}N_2OP$ (calcd.: 345.1157), found: 345.1151 ($[M+H]^+$). IR(film) *v* 3055, 2920, 2843, 1526, 1483, 1435, 1360, 1313, 1192, 1120, 1098, 997, 920, 847, 751, 705.

*(8-methylquinoxalin-2-yl)diphenylphosphine oxide(**5da-2**).* A brown solid, m.p.:206.8-207.1 °C (63 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.99-7.96 (m, 4H), 7.94 (d, *J* = 1.4 Hz, 1H), 7.75-7.71 (m, 1H), 7.63 (d, *J* = 7.0 Hz, 1H), 7.53 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.51 (t, *J* = 2.5 Hz, 1H), 7.45 (ddd, *J* = 7.1, 5.4, 2.4 Hz, 4H), 2.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6 (d, *J* = 125.9 Hz), 146.1 (d, *J* = 22.3 Hz), 142.9, 141.3 (d, *J* = 16.5 Hz), 138.4, 132.2 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 9.4 Hz), 131.3 (d, *J* = 128.0 Hz), 131.2, 128.5 (d, *J* = 12.2 Hz), 127.5 (d, *J* = 2.0 Hz), 17.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.13. HR-MS m/z (ESI): $C_{21}H_{18}N_2OP$ (calcd.: 345.1157), found: 345.1151 ($[M+H]^+$). IR(film) *v* 3047, 2915, 2843, 1569, 1480, 1435, 1329, 1257, 1192, 1158, 1120, 1100, 1050, 927, 829, 782, 748, 689.

*(6,7-dimethylquinoxalin-2-yl)diphenylphosphine oxide(**5ea**).* A yellow solid, m.p.: 124.1-125.6 °C (31 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.98-7.93 (m, 4H), 7.89 (s, 2H), 7.56-7.52 (m, 2H), 7.47 (ddd, *J* = 7.1, 5.3, 2.3 Hz, 4H), 2.49 (d, *J* = 9.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.6 (d, *J* = 126.2 Hz), 145.6 (d, *J* = 22.4 Hz), 143.1, 141.6 (d, *J* = 2.3 Hz), 141.5, 141.19 (d, *J* = 17.3 Hz), 132.0, 131.9, 131.62 (d, *J* = 104.5 Hz), 128.9, 128.4 (d, *J* = 12.3 Hz), 20.5, 20.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.54. HR-MS m/z (ESI): $C_{22}H_{19}N_2OPNa$ (calcd.: 381.1133), found: 381.1125 ($[M+Na]^+$). IR (film) *v* 3051, 2920, 2847, 1622, 1482, 1434, 1354, 1197, 1175, 1110, 866, 750, 721, 695.

*(6,7-dimethylquinoxalin-2-yl)di-m-tolylphosphine oxide(**5fc**).* A yellow solid, m.p.: 132.8-134.6 °C (61 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H), 7.89 (s, 2H), 7.78 (d, *J* = 12.5 Hz, 2H), 7.71 (dd, *J* = 12.5, 5.0 Hz, 2H), 7.38 – 7.35 (m, 4H), 2.49 (d, *J* = 9.2 Hz, 6H), 2.37 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9 (d, *J* = 125.6 Hz), 145.7 (d, *J* = 22.3 Hz), 143.1, 141.7 (d, *J* = 2.3 Hz), 141.5, 141.33 (d, *J* = 17.2 Hz), 138.4 (d, *J* = 12.2 Hz), 133.0 (d, *J* = 2.9 Hz), 132.4 (d, *J* = 9.4 Hz), 131.5 (d, *J* = 104.1 Hz), 129.3 (d, *J* = 9.8 Hz), 129.0, 128.4, 128.3, 21.5, 20.6, 20.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.19. HR-MS m/z (ESI): $C_{24}H_{23}N_2OPNa$ (calcd.: 409.1446), found: 409.1437 ($[M+Na]^+$). IR (film) *v* 3043, 2919, 2851, 1618, 1481, 1355, 1189, 1171, 1108, 1000, 869, 783, 693.

*(6,7-dimethylquinoxalin-2-yl)bis(4-fluorophenyl)phosphine oxide(**5fg**).* A yellow solid, m.p.: 134.1-135.6 ^{o}C (46 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.54 (s, 1H), 7.97 (ddd, *J* = 11.6, 8.6, 5.6 Hz, 4H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.18 (dd, *J* = 11.7, 4.8 Hz, 4H), 2.52 (d, *J* = 7.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (dd, *J* = 254.2, 3.3 Hz), 150.1 (d, *J* = 128.6 Hz), 145.5 (d, *J* = 22.5 Hz), 142.7 (d, *J* = 157.1 Hz), 141.8 (d, *J* = 2.3 Hz), 141.2 (d, *J* = 17.4 Hz), 134.6 (dd, *J* = 11.0, 8.9 Hz), 128.9 (d, *J* = 0.9 Hz), 128.5 (d, *J* = 1.9 Hz), 127.6 (dd, *J* = 108.2, 3.4 Hz), 116.0 (dd, *J* = 21.4, 13.5 Hz), 20.6, 20.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.07. HR-MS m/z (ESI): $C_{22}H_{17}F_2N_2OPNa$ (calcd.: 417.0944), found: 417.0935 ($[M+Na]^+$). IR (film) *v* 3055, 2931, 2847, 1593, 1500, 1357, 1237, 1162, 1118, 1061, 830.

*(6,7-dimethylquinoxalin-2-yl)bis(3-fluorophenyl)phosphine oxide(**5fh**).* A yellow solid, m.p.: 132.6-133.5 ^{o}C (32 mg, 35% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 7.92 (d, *J* = 2.4 Hz, 2H), 7.77 (dd, *J* = 11.5, 7.7 Hz, 2H), 7.69 (dd, *J* = 15.1, 6.0 Hz, 2H), 7.51-7.45 (m, 2H), 7.26 (dd, *J* = 15.4, 7.0 Hz, 2H), 2.52 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (dd, *J* = 250.4, 17.4 Hz), 149.4 (d, *J* = 129.2 Hz), 145.5 (d, *J* = 22.6 Hz), 143.7 , 142.1 , 142.0 (d, *J* = 2.3 Hz), 141.2 (d, *J* = 17.7 Hz), 134.0 (dd, *J* = 104.2, 5.8 Hz), 130.6 (dd, *J* = 14.3, 7.4 Hz), 128.7 (d, *J* = 42.3 Hz), 127.7 (dd, *J* = 8.8, 3.3 Hz), 119.6 (dd, *J* = 21.2, 2.5 Hz), 118.9 (dd, *J* = 22.8, 10.4 Hz), 20.7, 20.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.18 (t, *J* = 6.0 Hz). HR-MS m/z (ESI): $C_{22}H_{17}F_2N_2OPNa$ (calcd.: 417.0944), found: 417.0936 ($[M+Na]^+$). IR (film) *v* 3055, 2911, 2843,1581, 1477, 1420, 1356, 1269, 1220, 1174, 1094, 866, 793, 686.

*General Procedure for the reductive addition of diarylphosphine oxides with quinoline to Access compounds (**8**): (1,2,3,4-tetrahydroquinoline-2,4-diyl)bis(diphenylphosphine oxide) (**8aa**).* To a 5 mL vial equipped with oxygen balloon was added quinoline (**7a**, 25.8 mg, 0.2 mmol) and diphenylphosphine oxide (**2a**, 80.8 mg, 0.4 mmol). The reaction was then heated to 65 ^{0}C for 18 hours until the complete consuming of starting materials monitored by TLC. After being cooling down, the mixtures were quenched by adding water, and then extracted with ethyl acetate (3 mL×2). The crude product was purified on flash chromatography, with ethyl acetate/petroleum ether (1:1) as eluents to afford product **8aa** as a white solid (85 mg, 80% yield). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 13.9, 4.9 Hz, 4H), 7.72-7.65 (m, 2H), 7.61-7.33 (m, 14H), 6.93 (t, *J* = 7.7 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 1H), 6.29 (t, *J* = 7.4 Hz, 1H), 6.08 (d, *J* = 7.6 Hz, 1H), 4.93 (d, *J* = 12.3 Hz, 1H), 4.11 (s, 1H), 3.77-3.74 (m, 1H), 2.48 (t, *J* = 11.1 Hz, 1H), 2.21-2.04 (m, 1H). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 31.88, 30.56. HR-MS m/z (ESI): $C_{33}H_{29}NO_2P_2Na$ (calcd.: 556.1571), found: 556.1579 ($[M+Na]^+$).

*General Procedure for the reductive addition of diarylphosphine oxides with quinazoline to Access compounds (**10**): (1,2-dihydroquinazolin-2-yl)diphenylphosphine oxide(**10aa**).* To a 5 mL vial equipped with oxygen balloon was added quinazoline (**9a**, 26.0 mg, 0.2 mmol) and diphenylphosphine oxide (**2a**, 80.8 mg,

0.4 mmol). The reaction was then heated to 65 0C for 18 hours until the complete consuming of starting materials monitored by TLC. After being cooling down, the mixtures were quenched by adding water, and then extracted with ethyl acetate (3 mL×2). The crude product was purified on flash chromatography, with ethyl acetate as eluent to afford product **10aa** as awhite solid (62 mg, 93% yield). ^{1}H-NMR (400 MHz, CDCl3) δ 7.92 (dd, J = 9.8, 8.4 Hz, 2H), 7.71-7.66 (m, 2H), 7.52-7.40 (m, 6H), 7.07 (s, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 1H), 6.20 (d, *J* = 7.4 Hz, 1H), 5.66 (d, *J* = 5.0 Hz, 1H). ^{31}P-NMR (162 MHz, $CDCl_3$) δ 29.61. HR-MS m/z (ESI): $C_{20}H_{18}N_2OP$ (calcd.: 333.1157), found: 333.1151 ($[M+H]^+$).

■ AUTHOR INFORMATION

§ These authors contributed equally to this work.

Corresponding Author

**EMAIL: rickywu@njau.edu.cn*

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGEMENTS

This project is supported by the Foundation Research Project of Jiangsu Province (The Natural Science Found No. BK20141359), and "333 high level talent project" of JiangSu Province.

■ SUPPORTING INFORMATION

Supporting Information: [Experimental details and procedures, compound characterization data, and copies of ^{1}H, ^{13}C, ^{31}P NMR and HR-MS for all new compounds]. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ REFERENCES

(1) (a) Goldman, A. S. *Nature*, **1993**, *366*, 514-514; (b) Chen, H. Y.; Shlecht, S.; Semple, T. C.; Hartwig, J. F. *Science*, **2000**, *287*, 1995-1997; (c) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731-1769; (d) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624-655; (e) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293-1314; (f) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315-1345; (g) Engel, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788-802; (h) Wencel-Delord, J.; Glorius, F. *Nat. Chem.* **2013**, *5*, 369-375; (i) Guo, X.-X.; Gu, D.-W.; Wu, Z.; Zhang,W. *Chem. Rev.* **2015**, *115*, 1622-1651.

(2) (a) Li, C. J. *Acc. Chem. Res.* **2009**, *42*, 335-344; (b) Scheuermann, C. J. *Chem. Asian J.* **2010**, *5*, 436-451; (c) Pintér, A.; Sud, A.; Sureshkumar, D.; Klussmann, M. *Angew. Chem. Int. Ed.* **2010**, *49*, 5004-5007.

(3) (a) Li, Z. P.; Li, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 3672-3673; (b) Li, Z. P.; Bohle, D. S.; Li, C. J. *Proc. Natl. Acad. Sci. U. S. A.*, **2006**, *103*, 8928-8933; (c) Baslé, O.; Li, C. J. *Green Chem.* **2007**, *9*, 1047-1050; (d) Zhao, L.; Li, C. J. *Angew. Chem. Int. Ed.* **2008**, *47*, 7075-7078; (e) Basle, O.; Borduas, N.; Dubios, P.; Chapuzet, J. M.; Chan, T.-H.; Lessard, J.; Li, C. J. *Chem. Eur. J.* **2010**, *16*, 8162-8166, and references cited herein.

(4) (a) Sud, A.; Sureshkumar, D.; Klussmann, M. *Chem. Commun.* **2009**, 3169-3171; (b) Pintér, A.; Klussmann, M. *Adv. Synth. Catal.* **2012**, *354*, 701-711; (c) Schweitzer-Chaput, B.; Stud, A.; Pintér, A.; Dehn, S.; Schulze, P.; Klussmann, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 13228-13232.

(5) (a) Shi, W.; Liu, C.; Lei, A. *Chem. Soc. Rev.* **2011**, *40*, 2761-2776; (b) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780-1824, and references cited herein.

(6) (a) Shi, Z. Z.; Zhang, C.; Li, S.; Pan, D.; Ding, S.; Cui, Y.; Jiao, N. *Angew. Chem. Int. Ed.* **2009**, *48*, 4572-4576; (b) Shi, Z.; Zhang, C.; Tang, C.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3381-3430, and references cited herein.

(7) (a) Huang, H.; Ji, X.; Tang, X.; Zhang, M.; Li, X.; Jiang, H. *Org. Lett.* **2013**, *15*, 6254-6257; (b) Jiang, H.; Yang, W.; Chen, H.; Li, J.; Wu, W. *Chem. Commun.* **2014**, *50*, 7202-7204;

(8) (a) Li, Z. P.; Cao, L.; Li, C. J. *Angew. Chem. Int. Ed.* **2007**, *46*, 6505-6507; (b) Li, Z. P.; Li, H.; Guo, X.; Cao, L.; Yu, R.; Li, H.; Pan, S. *Org. Lett.* **2008**, *10*, 803-805; (c) Xi, P. H.; Yang, F.; Qin, S.; Zhao, D.; Lan, J.; Gao, G.; Hu, C.; You, J. *J. Am. Chem. Soc.* **2010**, *132*, 1822-1824; (d) Graczyk, K.; Ma, W.; Ackermann, L. *Org. Lett.* **2012**, *14*, 4110-4113; (e) Zhang, G.; Ma, Y.; Wang, S.; Zhang, Y.; Wang, R. *J. Am. Chem. Soc.* **2012**, *134*, 12334-12337; (f) Ueda, H.; Yoshida, K.; Tokuyama, H. *Org. Lett.* **2014**, *16*, 4194-4197; (g) Xu, Q. L.; Gao, H.; Yousufuddin, M.; Ess, D. H.; Kürti, L. *J. Am. Chem. Soc.* **2013**, *135*, 14048-14051; (h) Huo, C.; Yuan, Y.; Wu, M.; Jia, X.; Wang, X.; Chen, F.; Tang, J. *Angew. Chem. Int. Ed.* **2014**, *53*, 13544-13547; (i) Kumar, S.; Rathore, V.; Verma, A.; Prasad, C. D.; Kumar, A.; Yadav, A.; Jana, S.; Sattar, M.; Meenakshi; Kumar, S. *Org. Lett.* **2015**, *17*, 82-85.

(9) (a) Lin, R. Y.; Chen, F.; Jiao, N. *Org. Lett.* **2012**, *14*, 4158-4161; (b) Lu, Q.; Zhang, J.; Zhao, G.; Qi, Y.; Wang, H.; Lei, A. *J. Am. Chem. Soc.* **2013**, *135*, 11481-11484; (c) Lu, Q. Q.; Zhang, J.; Wei, F.; Qi, Y.; Wang, H.; Liu, Z.; Lei, A. *Angew. Chem. Int .Ed.* **2013**, *52*, 7156-7159; (d) Kamal, A.; Reddy, D. R.; Rajendar, *J. Mol. Catal. A: Chem.* **2007**, *272*, 26-30.

(10) Wu, K.; Huang, Z.; Liu, C.; Zhang, H.; Lei, A. *Chem. Commun.* **2015**, *51*, 2286-2289.

(11) For selected C(sp^2)-P formation *via* oxidative coupling catalyzed by transition metals, see: (a) Kuninobu, Y.; Yoshida,T. and Takai, K. *J. Org. Chem*. **2011**, *76*, 7370-7376; (b) Hou, C. D.; Ren, Y. L.; Lang, R.; Hu, X. X.; Xia, C. G.; Li, F. W. *Chem. Commun.* **2012**, *48*, 5181-5183; (c) Xiang, C.-B.; Bian, Y.-J.; Mao, X.-R.; Huang, Z.-Z. *J. Org. Chem.* **2012**, *77*, 7706-7710; (d) Feng, C.-G.; Ye, M.; Xiao, K.-J.; Li, S. and Yu, J.-Q. *J. Am.*

Chem. Soc. **2013**, *135*, 9322-9325; (e) Li, C.-K.; Yano, T.; Ishida, N. and Murakami, M. *Angew. Chem., Int. Ed*., **2013**, *52*, 9801-9804; (f) Mi, X.; Huang, M.; Zhang, J.; Wang, C. and Wu, Y. *Org. Lett*., **2013**, *15*, 6266-6269; (g) Zhou, A.-X.; Mao, L.-L.; Wang, G.-W.; Yang, S.-D. *Chem. Commun.* **2014**, *50*, 8529-8532; (h) Zhang, H.-J.; Lin, W.-D.; Wu, Z.-J.; Ruan, W.-Q.; Wen, T.-B. *Chem. Commun.* **2015**, *51*, 3450-3453.

(12) For selected books and reviews: (a) Quin, L. D. A Guide to Organophosphorus Chemistry, John Wiley & Sons, New York, **2000**; (b) Van der Jeught, S.; Stevens, C. V. *Chem. Rev.* **2009**, *109*, 2672-2702. (c) Demmer, C. S.; Krogsgaard-Larsen, N.; Bunch, L. *Chem. Rev.* **2011**, *111*, 7981-8006; (d) Queffélec, C.; Petit, M.; Janvier, P.; Knight, D. A.; Bujoli, B. *Chem. Rev.* **2012**, *112*, 3777-3807; (e) Montchamp, J. L. *Acc. Chem. Res*. **2014**, *47*, 77-87.

(13) (a) Han, L.-B.; Tanaka, M. *J. Am. Chem. Soc.* **1996**, *118*, 1571-1572. (b) Han, L.-B.; Zhang, C.; Yazawa, H.; Shimada, S. *J. Am. Chem. Soc.* **2004**, *126*, 5080-5081. (c) Chen, Y.-R.; Duan, W.-L. *J. Am. Chem. Soc.* **2013**, *135*, 16754-16757.

(14) (a) Kalek, M.; Johansson, T.; Jezowska, M.; Stawinski, J. *Org. Lett.* **2010**, *12*, 4702-4704. (b) Kalek, M.; Stawinski, J. *Adv. Synth. Catal*. **2011**, *353*, 1741-1755.

(15) Gui, Q.-W.; Hu, L.; Chen, X.; Liu, J.-D.; Tan, Z. *Chem. Commun*. **2015**, *51*, 13922-13924.

(16) (a) Andaloussi, M.; Lindh, J.; Savmarker, J.; Sjöberg, P. J. R.; Larhed, M. *Chem. Eur. J.* **2009**, *15*, 13069-13074. (b) Zhuang, R.; Xu, J.; Cai, S.; Tang, G.; Fang, M.; Zhao, Y. *Org. Lett.* **2011**, *13*, 2110-2113.

(17) (a) Bloomfield, A. J.; Herzon, S. B. *Org. Lett.* **2012**, *14*, 4370-4373. (b) Shen, C.-R.; Yang, G.-Q.; Zhang, W.-B. *Org. Biomol. Chem.* **2012**, *10*, 3500-3505; (c) Fu, W.-C.; So, C.-M.; Kwong, F.-Y. *Org. Lett.* **2015**, *17*, 5906-5909.

(18) Chen, X.-L.; Li, X.; Qu, L.-B.; Tang, Y.-C.; Mai, W.-P.; Wei, D.-H.; Bi, W.-Z.; Duan, L.-K.; Sun, K.; Chen, J.-Y.; Ke, D.-D.; Zhao, Y.-F. *J. Org. Chem.* **2014**, *79*, 8407-8416.

(19) Luo, K.; Chen, Y.-Z.; Yang, W.-C.; Zhu, J.; Wu, L. *Org. Lett.* **2016**, *18*, 452-455.

(20) (a) Chen, Y.-Z.; Zhang, L.; Lu, A.-M.; Yang, F.; Wu, L. *J. Org. Chem.* **2015**, *80*, 673-680; (b) Liu, T.; Dong, J.; Cao, S.-J.; Guo, L.-C.; Wu, L. *RSC Adv.* **2014**, *4*, 61722-61726; (c) Liu, T.; Xia, Y.-T.; Zhu, J.; Lu, A.-M.; Wu, L. *Tetrahedron Lett.* **2015**, *56*, 6508-6512; (d) Wu, L.; Zhang, X.; Chen, Q.-Q.; Zhou, A.-K. *Org. Biomol. Chem.* **2012**, *10*, 7859-7862; (e) Wu, L.; Zhang, X.; Tao, Z. *Catal. Sci. Tech.* **2012**, *2*, 707-710; (f) Wu, L.; Ling, J.; Wu, Z.-Q. *Adv. Synth. Catal.* **2011**, *353*, 1452-1456.

(21) For similar reductive addition of P(O)-H compounds to *N*-heterocycles forming C(sp^3)-P bonds, see: (a) Blieck, A. D.; Masschelein K. G. R.; Dhaene, F.; Rozycka-Sokolowska, E.; Marciniak, B.; Drabowicz, J.; Stevens, C. V. *Chem. Commun.* **2010**, *46*, 258-260; (b) Gao, Y.-X.; Deng, H.-G.; Zhang, S.-S.; Xue, W.-H.; Wu, Y.-L; Qiao, H.-W.; Xu, P.-X.; Zhao, Y.-F. *J. Org. Chem.* **2015**, *80*, 1192-1199; (c) Zhang, Q.-Q.; Wei, D.-H.; Cui, X.-L.; Zhang, D.; Wang, H.; Wu, Y.-J. *Tetrahedron* **2015**, *71*, 6087-6093.

(22) (a) Aparicio, D.; Attanasi, O. A.; Filippone, P.; Ignacio, R.; Lillini, S.; Mantellini, F.; Palacios, F.; de los Santos, J. M. *J. Org. Chem.* **2006**, *71*, 5897-5905; (b) Adam, M. S. S.; Mohamad, A. D.; Jones, P. G.; Kindermann, M. K.; Heinicke, J. W. *Polyhedron*, **2013**, *50*, 101-111; (c) Yang, J.; Chen, T. Q.; Han, L.-B. *J. Am. Chem. Soc.* **2015**, *137*, 1782-1785.