JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b00570 • Publication Date (Web): 16 May 2019

Just Accepted

ACS Publications

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

A Photoredox/Cobalt-Catalyzed Phosphinyloxy Radical Addition/Cyclization Cascade: Synthesis of Phosphaisocoumarins

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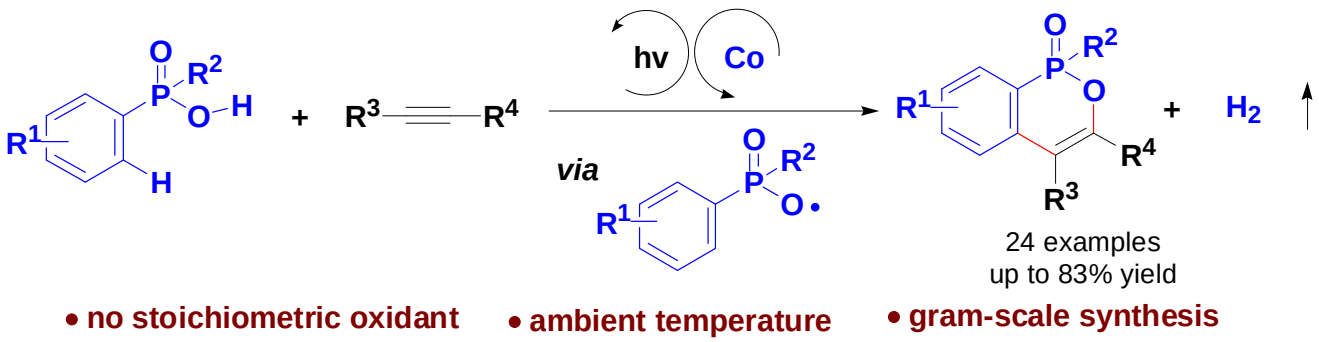


Abstract

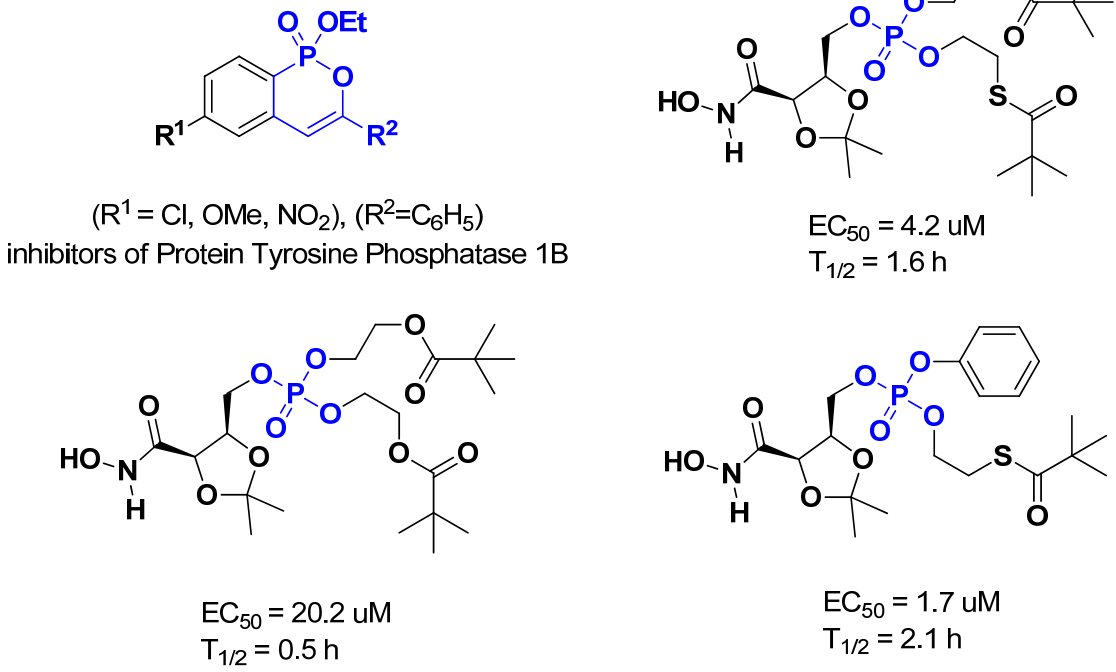
A novel visible-light photoredox catalyzed phosphinyloxy radical addition/cyclization cascade of arylphosphinic acids or arylphosphonic acid monoesters with alkynes has been developed, which provides an efficient and practical access to various phosphaisocoumarins by using a dual catalytic system containing an acridinium photosensitizer and a cobaloxime proton-reducing catalyst,

[Co(dmgH)$_2$]PyCl at ambient temperature. This method has advantages of broad substrate scope, mild condition as well as without any sacrificial oxidant.

Introduction

Organophosphorus compounds are of great importance not only in many functional materials and bioactive fine chemicals, such as agrochemicals, pharmaceuticals and natural products, [1] but also as synthetic reagents in organic synthesis, versatile phosphine ligands in transition metal catalysis or nucleophilic organo-catalysts.[2] Generally speaking, phosphorus substituents can regulate important biological, medicinal and materials functions, so, heterocycles containing phosphorus or phosphonyl group are received considerable attention to organic and medicinal chemists (**Figure 1**). [1]

Figure 1. Some important biologically active P-containing molecules.



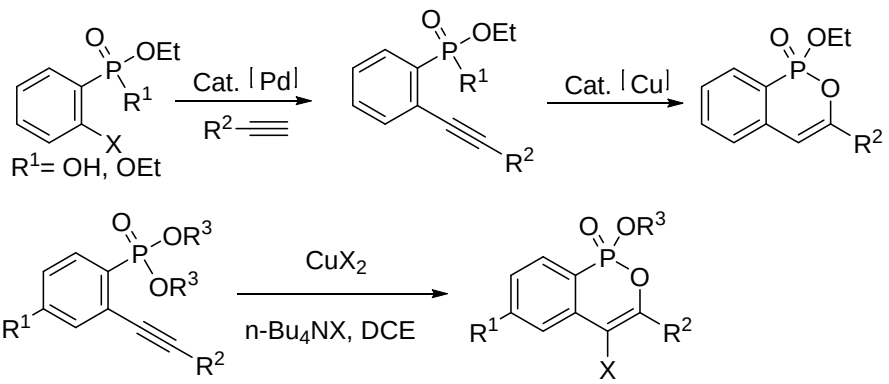
Phosphaisocoumarin, as a phosphorus analogue of isocoumarins, displayed versatile and interesting biological activies.[3] In 2013, Ding group first reported the preparation of phosphaisocoumarins by Cu(I)-catalyzed intramolecular cyclization of *o*-ethynylphenylphosphonic acid monoesters (**Scheme**

1a).[4a] After that, Peng reported the CuX_2 (X = Br, Cl) mediated direct halocyclization for the synthesis of 4-halophosphaisocoumarins **(Scheme 1a**).[4b] Afterwards, Lee developed rhodium- and ruthenium-catalyzed oxidative C–H activation/cyclization for the synthesis of phosphaisocoumarins using arylphosphinic acids or arylphosphonic acid monoesters and alkynes as the starting materials (**Scheme 1b)**.[5] Despite these remarkable advances, in order to achieve good yields, stoichiometric oxidant or elevated temperature is usually required in these transformations. In this regard, the development of an efficient and environmentally benign method for the synthesis of phosphaisocoumarins is still highly desirable.

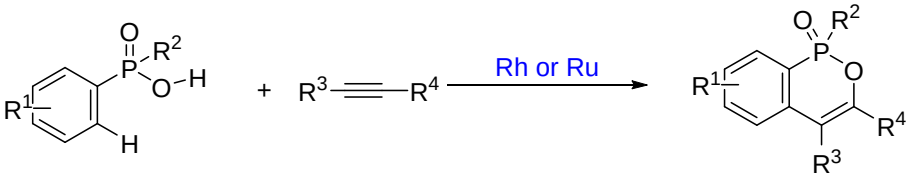
Recently, visible-light photoredox catalysis has attracted increasing research interest from synthetic community due to its extremely mild condition and environmental friendly character,[6] and a photoredox/cobaloxime dual catalytic system provides a new strategy for the construction of a variety of heterocycles without external oxidants.[7] Herein, we developed an unprecedented visible-light photoredox-catalyzed phosphinyloxy radical formation by O−H cleavage of arylphosphinic acids or arylphosphonic acid monoesters with H_2 release in the presence of a cobalt catalyst, and its application in the synthesis of a variety of phosphaisocoumarins through the phosphinyoxy radical addition/cyclization with alkynes in high atom-economy at ambient temperature is accomplished (**Scheme 1c**).

Scheme 1 Preparation of phosphaisocoumarins

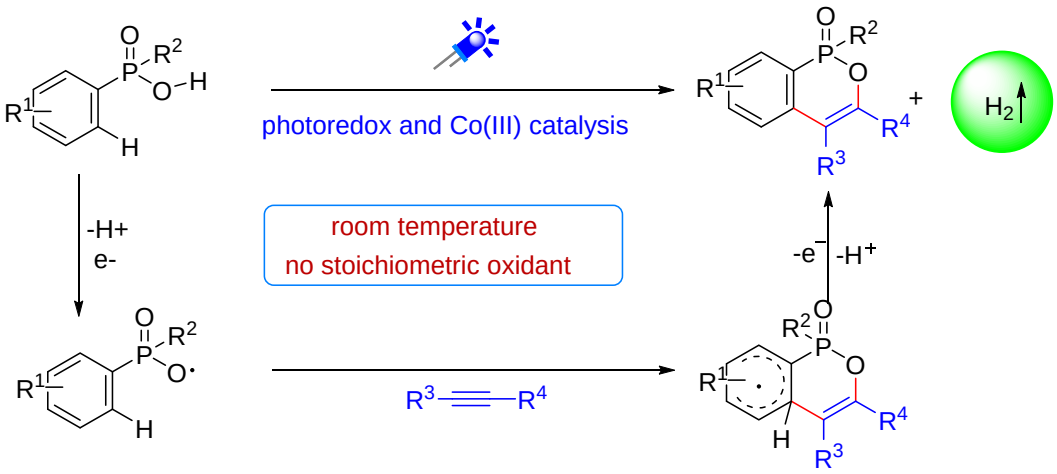
(a) Ding and Peng's work:



(b) Lee's work:



(c) This work: photoredox catalyzed phosphinyloxy radical addition/cyclization cascade

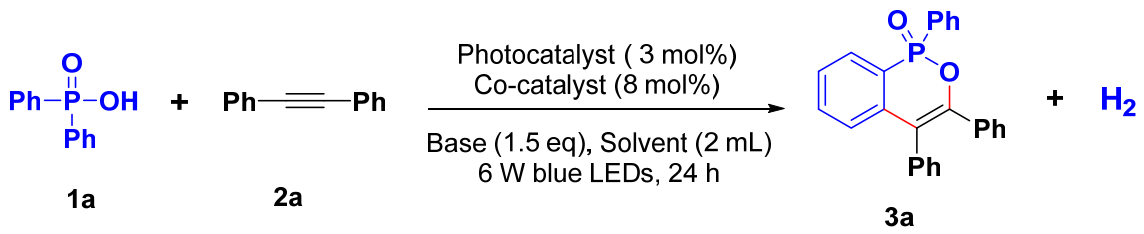


Results and Discussion

Initially, diphenylphosphinic acid **1a** and diphenylacetylene **2a** were chosen as the model substrates and CsF as the base under irradiation of 6 W blue LEDs in the presence of Acr^{+}-$MesClO_4^{-}$ (3 mol%) and $[Co(dmgH)_2]PyCl$ (8 mol%) (**Table 1**). To our delight, this reaction indeed proceeded, delivering the desired product **3a** in 46% NMR yield (**Table 1**, entry 1). The structure of **3a** was unambiguously confirmed by X-ray single-crystal diffraction analysis.[8] A variety of bases were evaluated, it's found that CsF was still the best choice for this transformation (**Table 1**, entries 1–3). The mixture of

chloroform and water (*V/V*, 4:1) can improve the yield of **3a** to 52% (**Table 1,** entry 4). By screening photo-catalysts and Co(III) catalysts, it is found that other Co(III) catalysts, such as $Co(dmgH)_2(4\text{-}NMe_2Py)Cl$, $Co(dmgH)_2(4\text{-}CO_2MePy)Cl$, and $[Co(dmgH)_2Py_2]PF_6$ are less effective (**Table 1**, entries 5-7), and other photocatalysts, such as $Ru(bpz)_3(PF_6)_2$ and *fac*-$Ir(ppy)_3$ can not tigger the reaction (**Table 1**, entries 8-9). DiRocco[9] and Nicewicz[10] found that Acr^+-$MesClO_4^-$ can undergo demethylation and is prone to nucleophilic attack, which can lead to lose the photocatalytic activity. To our delight, when the reaction was carried out for 24 h, extra Acr^+-$MesClO_4^-$ (3 mol%) was added to the reaction mixture and continued to be stirred until 48 h, the product **3a** can improve to 72% isolated yield (**Table 1**, entry 10). Control experiments indicated that without the photocatalyst, base or visible light irradiation, the reaction did not occur, indicating that visible light, base and photocatalyst were essential for this reaction. Moreover, the addition of the cobalt catalyst $[Co(dmgH)_2]PyCl$ can improve the reaction efficiency (see **Supporting Information**).

Table 1. Optimization of reaction condition[a]



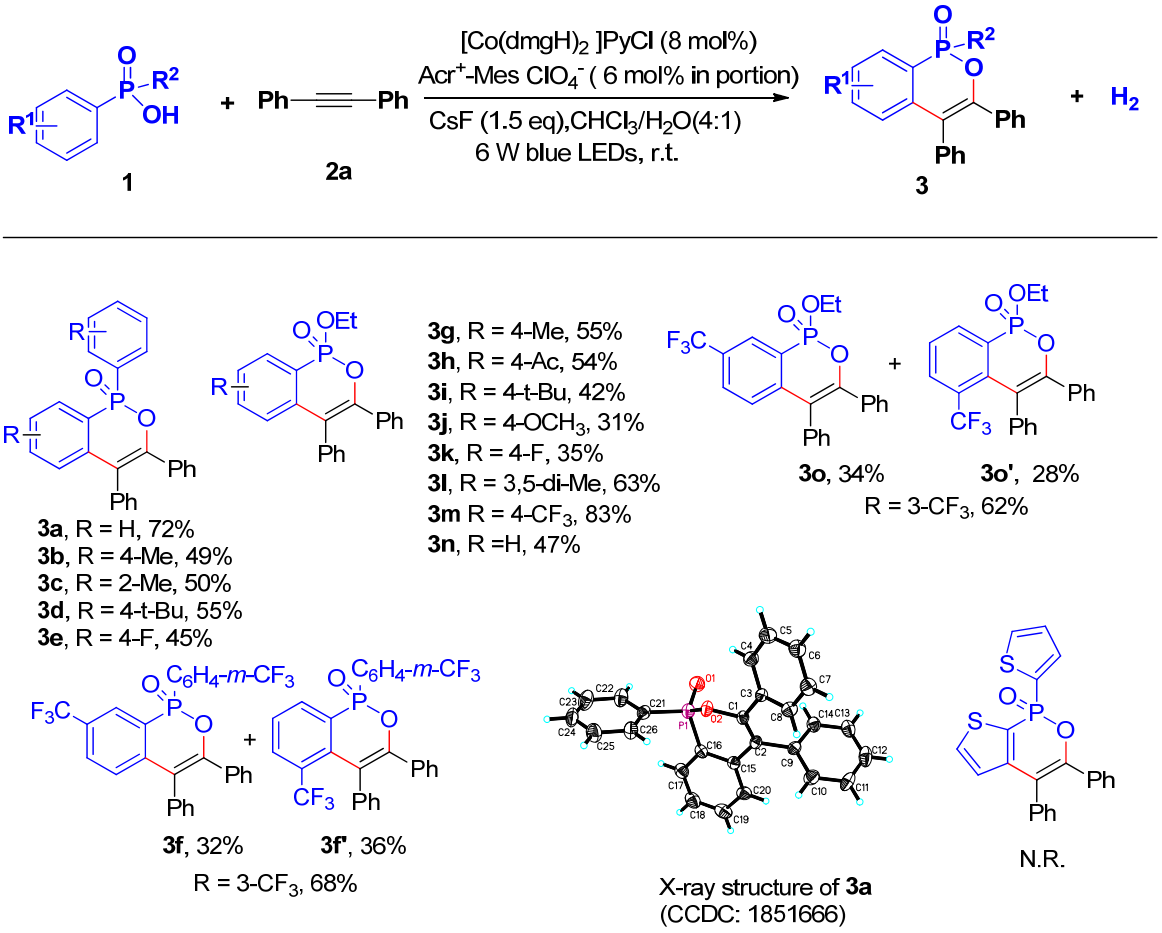
entry	photocatalyst	solvent	base	Co(III) catalyst	yield[b] (%)
1	Acr^+-Mes ClO_4^-	$CHCl_3$	CsF	$[Co(dmgH)_2]PyCl$	46
2	Acr^+-Mes ClO_4^-	$CHCl_3$	DMAP	$[Co(dmgH)_2]PyCl$	Trace
3	Acr^+-Mes ClO_4^-	$CHCl_3$	Cs_2CO_3	$[Co(dmgH)_2]PyCl$	15
4	Acr^+-Mes ClO_4^-	$CHCl_3/H_2O$（4:1）	CsF	$[Co(dmgH)_2]PyCl$	52
5	Acr^+-Mes ClO_4^-	$CHCl_3/H_2O$ (4:1）	CsF	$Co(dmgH)_2(4\text{-}NMe_2Py)Cl$	29
6	Acr^+-Mes ClO_4^-	$CHCl_3/H_2O$ (4:1）	CsF	$Co(dmgH)_2(4\text{-}CO_2MePy)Cl$	32

7	Acr^+-Mes ClO_4^-	$CHCl_3/H_2O$ (4:1)	CsF	$[Co(dmgH)_2Py_2]PF_6$	33
8	$Ru(bpz)_3(PF_6)_2$	$CHCl_3/H_2O$ (4:1)	CsF	$[Co(dmgH)_2]PyCl$	Trace
9	*fac*-$Ir(ppy)_3$	$CHCl_3/H_2O$ (4:1)	CsF	$[Co(dmgH)_2]PyCl$	N.R.
10[c, d]	**Acr^+-Mes ClO_4^-**	**$CHCl_3/H_2O$** (4:1)	**CsF**	**$[Co(dmgH)_2]PyCl$**	**72**

[a]**1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv.), photocatalyst (0.006 mmol, 3 mol%), base (0.3 mmol, 1.5 equiv.), Co(III) catalyst (0.016 mmol, 8 mol%), 2.0 mL of solvent, 6 W blue LEDs, 24 h. [b]determined by ^{31}P NMR analysis using trioctylphosphine oxide as an internal standard. [c]Acr^+-MesClO_4^- (5.0 mg, 0.012 mmol, 6 mol%) was added portionwise (3 mol% of PC was added first, after 24 h another 3 mol % of PC was added), 48 h. [d]isolated yield based on **1a** in parenthesis.

With the optimized reaction condition being established, the scope of arylphosphinic acids was then investigated. As highlighted in **Table 2,** substrates bearing either electron-donating groups (i.e., methyl-, *t*-Bu-) or electron-withdrawing group (i.e., fluoro-, CF_3-) on the benzene ring, either *ortho*-, *meta*- or *para*-substituted group, were found to be suitable for the reaction, delivering the corresponding products in moderate yields (45%-68%, **3b-3f**). It is worth noting that when 3-trifluoromethyl substituted phosphinic acid was employed, two products (**3f** and **3f'**) with *ortho*- and *para*-cyclization patterns can be isolated in 68% total yield. However, when heteroaryl-substituted phosphinic acids (e g., thiophene-substituted) were employed, unfortunately, the reaction did not occur. Encouraged by these results, to test the generality of the cascade reaction, we turned our attention to investigate whether a series of arylphosphonic acid monoesters could be acted as suitable candidates. As shown in **Table 2**, a series of arylphosphonic acid monoesters, either electron-donating groups (e. g., CH_3, OCH_3, *t*-Bu) or electron-withdrawing groups (e. g., F, CF_3 and acetyl), and different substituted pattern on the benzene ring, are compatible in the reaction, furnishing corresponding products **3g-3o** in moderate to high yields (**Table 2**, 31-83% yields). It is found that the electronic property of substituents on the benzene ring has some influence on the reaction efficiency, for example, 4-trifluoromethyl substituted substrate can give the best result (**3m**, 83% yield). Moreover, when 3-trifluoromethyl substituted substrate was adopted, two products (**3o** and **3o'**) with *ortho*- and *para*-cyclization can be isolated in 62% total yield.

Table 2. Substrate Scope of Arylphosphinic acids or Arylphosphonic Acid Monoesters[a,b]

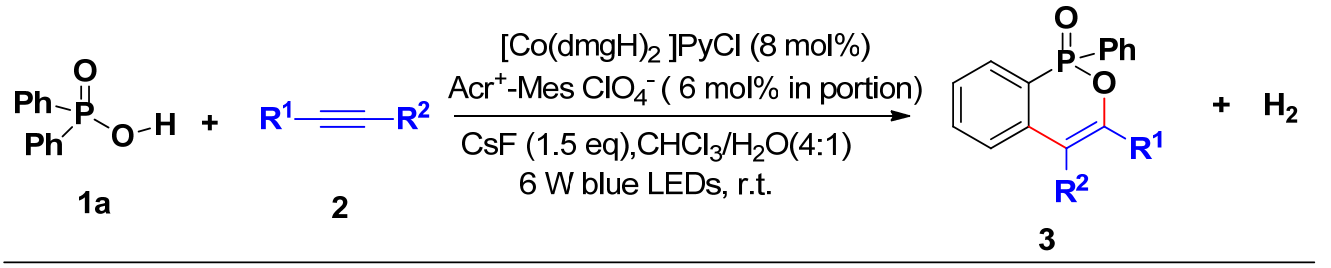


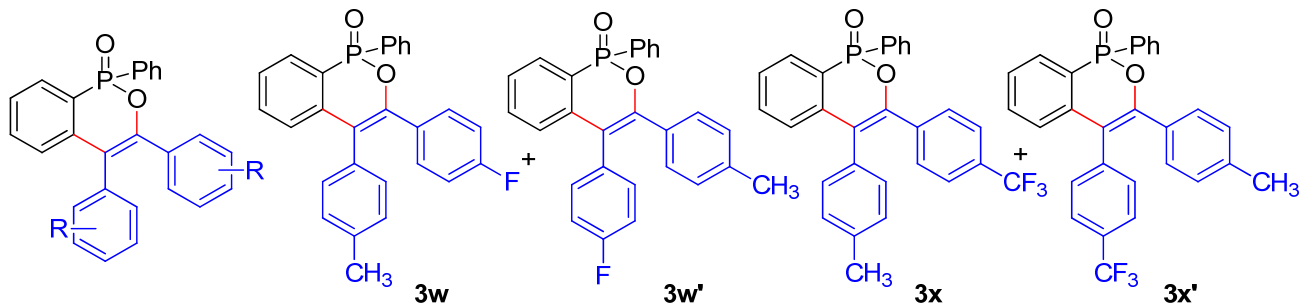
[a]Reaction condition from **Table 1**, entry 10, 0.2 mmol scale. [b] Isolated yield based on **1**.

Subsequently, we continued to evaluate the alkyne scope of the cascade reaction between diphenylphosphinic acid **1a** and a variety of alkynes **2**. As summarized in **Table 3**, various symmetric biaryl alkynes **2** were found to be compatible for the reactions and gave the desired products **3p-3v** in 25-71% yields. The electronic property of substituents on the benzene ring (e. g., -F, -Cl, -Me and -*t*-Bu) had no obvious influence on the reaction efficiency, and the corresponding products **3p-3u** were provided in moderate isolated yields (**Table 3**, 57-71% yields). Notably, the bromo-substituted substrate tolerated well in this reaction and gave the bromo-containing product **3v**, albeit in low yield (**Table 3**, 25% yield), which is usually incompatible in transition-metal-catalyzed reactions. As for unsymmetric alkynes, when the disubstituents on the phenyl rings of the diarylacetylenes were $-CF_3$ and $-CH_3$, $-F$ and $-CH_3$, respectively, the desired products **3w** and **3w′**, **3x** and **3x'** were isolated as the mixtures of

regio-isomers in 47-75% yields, the pure regio-isomers can be isolated further by HPLC, and their major isomers **3w** and **3x** were unambiguously confirmed by X-ray single-crystal diffraction analysis.[8] The observation of regioselectivity could be due to the distinctly biased electronic property on the alkynes. However, alkyl substituted alkynes, such as phenylacetylene, (2-phenylethynyl) trimethyl silane, phenyl prop-1-yne, and heterocycle-stituted alkynes, for example thiophene-substituted alkyne, are not active in the cascade reaction.

Table 3. Substrate Scope of Alkynes [a,b]





3p, R = 4-t-Bu, 71%
3q, R = 3,5-di-Me, 69%
3r, R = 4-Me, 57%
3s, R = 2-Me, 80%
3t, R = 4-F, 70%
3u, R = 4-Cl, 61%
3v, R = 4-Br, 25%

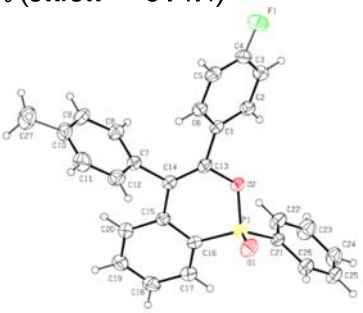
75% (**3w/3w'** = 3 : 1.4)

47% (**3x/3x'** = 3 : 1.3)

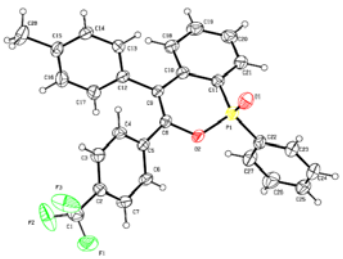
Some unsuccessful substrates:

Ph—≡ ; Ph—≡—TMS

Ph—≡—CH_3 trace



X-ray structure of **3w**
(CCDC: 1880620)



X-ray structure of **3x**
(CCDC: 1879737)

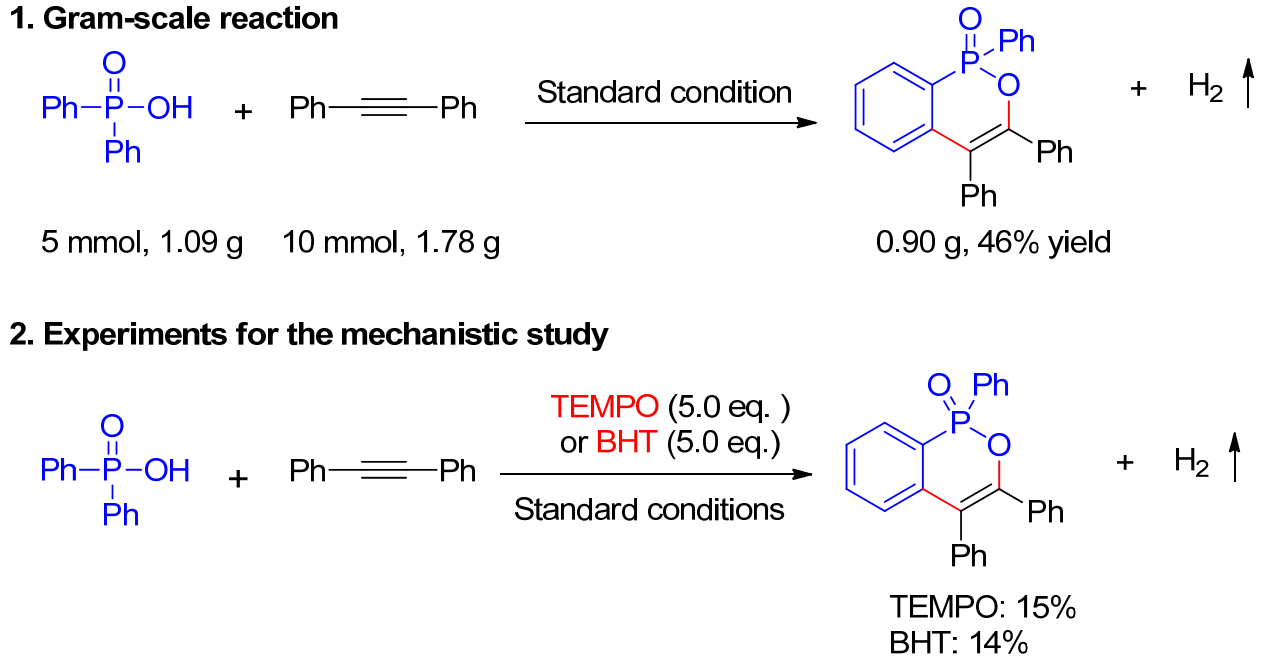
[a] Reaction condition from **Table 1**, entry 10, 0.2 mmol scale. [b] Isolated yield based on **1a**.

In order to demonstrate the potential synthetic application, a gram-scale reaction of **1a** with **2a** was performed under standard condition, the desired product **3a** was achieved in 46 % yield (0.90 g). To

gain further insight into the mechanism, when radical scavengers, such as TEMPO or BHT, were introduced to the model reaction of substrates **1a** and **2a** under standard condition, reaction efficiencies were partially inhibited, the desired compound **3a** was isolated in 15 % and 14% yield, respectively, without the observation of the products of phosphinyoxy radical being captured (**Scheme 2**).

The Luminescence quenching experiments showed that both **1a** with CsF, and diphenylacetylene **2a** could quench the excited photocatalyst $^{*}Acr^{+}$-$MesClO_4^{-}$ (see **Supporting Information**). A cyclic voltammogram indicated the oxidation potential of **1a** in the presence of CsF is 1.67 V *vs* SCE, which indicated that phosphinate of **1a** could be oxidized to phosphinyloxy radical **B** through single-electron transfer (SET) by the excited photocatalyst $^{*}Acr^{+}$-$Mes\,ClO_4^{-}$ ($E_{1/2red}$ [$Acr^{\bullet}$-$Mes^{\bullet+}$/$Acr^{\bullet}$-Mes] = +2.06 V *vs*. SCE). Moreover, the pathway that the acridine excited species can oxidize diphenylacetylene ($E_{1/2red}$ = +1.86 V *vs*. SCE) to an alkyne radical cation *via* a SET process is also possible.

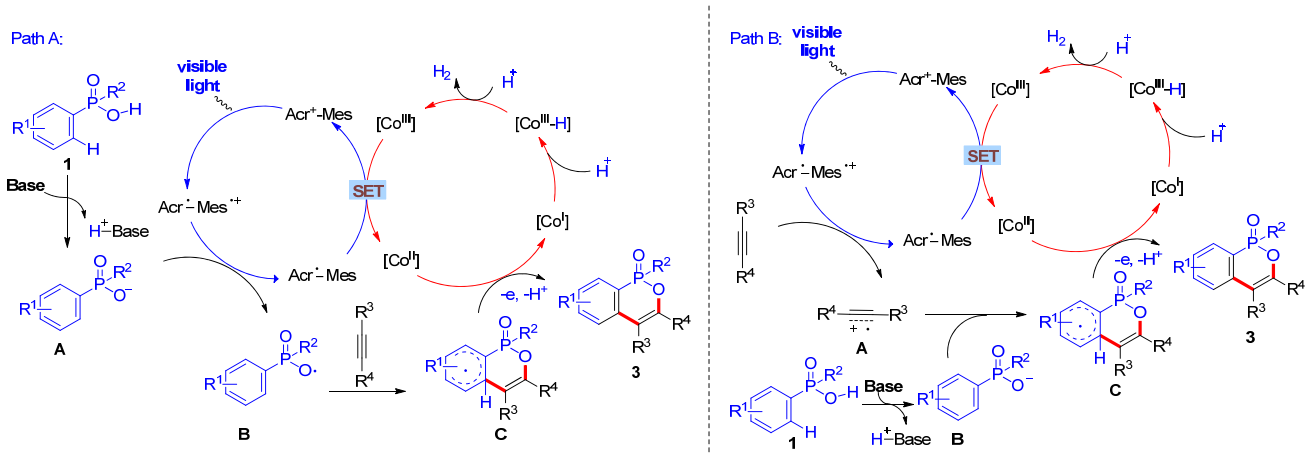
Scheme 2. **Gram-scale reaction and experiments for the mechanistic study**



On the basis of above observations (see **Supporting Information**) and some related literatures,[7i-j, 11] we proposed plausible mechanism for the phosphinyloxy radical-mediated radical addition/cyclization cascade reaction (**Figure 2**). In situ-generated anionic intermediate **A** is initially oxidized to the key phosphinyloxy radical **B** by the photoexcited state photocatalyst $^{*}Acr^{+}$-$MesClO_4^{-}$ *via* a SET process

(Path A), subsequent radical addition to alkyne and cyclization results in an aryl radical species and further oxidation by cobalt catalyst leads to the desired product **3**. The latter step may proceed through hydrogen atom abstraction (HAT) or electron/proton transfer sequence. The cobalt catalyst would act as the proton or electron reservoir, leading to hydrogen gas release.[7a, 7b, 7d, 11] However, the reduction of Co^{III}-H to Co^{II}-H, following by protonation to release H_2 or the homolytic cleavage involving two Co^{III}-H to evolve hydrogen gas can not be ruled out.[11, 12] On the other hand, the pathway that diphenylacetylene ($E_{1/2red}$ = +1.86 V *vs*. SCE) can be oxidized to an alkyne radical cation by the photoexcited state Acr$^+$-MesClO$_4^-$ ($E_{1/2red}$ [Acr$^{\bullet}$-Mes$^{\bullet+}$/Acr$^{\bullet}$-Mes] = +2.06 V *vs*. SCE) through a SET process (Path B) is also possible.[13]

Figure 2. Proposed Mechanism.



In conclusion, the first photoredox/cobalt-catalyzed phosphinyloxy radical addition/cyclization cascade for the synthesis of phosphaisocoumarins with high atom economy under ambient temperature was developed. This method has advantages of mild condition, with no use of any sacrificial oxidant as well as wide substrate scopes, which will inspire the application of phosphinyloxy radical mediated synthetic transformations by visible light irradiation for the synthesis of structurally diversity phosphorus heterocycles.

Experimental Section

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. The solvents used were purified by distillation over the drying agents. All of the

reactions were monitored by analytical thin layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400/600 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 ppm) for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C{^{1}H}NMR spectra were recorded on Varian Mercury 400 (100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). HRMS was recorded on Bruker ultrafleXtreme MALDITOF/TOF mass spectrometer. All of the reactions were carried out using a schlenk borosilicate reaction tube (10 mL) flask without special photochemical equipment. There is 5.0 cm distance between the reactor and LEDs. The cobalt complexes $Co(dmgH)_2(4\text{-}NMe_2Py)Cl$, $Co(dmgH)_2(4\text{-}CO_2MePy)Cl$, $Co(dmgH)_2(4\text{-}CONEt_2Py)Cl$ and $[Co(dmgH)_2Py_2]PF_6$ were prepared according to the reported procedure.[14]

All alkynes **2** are known compounds, which were synthesized according to the reported method.[15] *1-Methyl-4-[(p-tolyl) ethynyl] benzene (**2r**)*(known compound).[15] A white solid; yield 670 mg (65%); mp 137 - 139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.41 (d, J = 7.7 Hz, 4H), 7.14 (d, J = 7.6 Hz, 4H), 2.35 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 138.1, 131.4, 129.1, 120.3, 88.8, 21.6.

All diarylphosphinic acids **1** are known compounds, which were synthesized according to the reported method [16]. *Bis (4-tert-butyl) phenylphosphinic acid (**1d**)*(known compound).[16] A white solid; yield 908 mg (55%); mp 200 - 202 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.58 (s, 1H), 7.67 (dd, J = 12.2, 8.1 Hz, 4H), 7.38 (dd, J = 8.4, 3.1 Hz, 4H), 1.29 (s, 18 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 155.0 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.9 Hz), 129.8 (d, $J_{C\text{-}P}$ = 141.6 Hz), 125.2 (d, $J_{C\text{-}P}$ = 13.0 Hz), 34.9, 31.1.

Arylphosphonic mono-ester were synthesized according to the reported procedure [5c]. Except for **1g**, **1i**, **1l**, **1m** and **1o** are new compounds, other arylphosphonic mono-esters are kown compounds.

*(4-Methoxy phenyl) phosphonic acid monoethyl ester (**1j**)*(known compound).[5c] A yellow oil; yield 71.3 mg (66 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 11.56 (s, 1H), 7.76-7.63 (m, 2H), 6.99-6.78 (m, 2H), 4.14-3.93 (m, 2H), 3.82 (s, 3H), 1.27 (q, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 162.6 (d, J_{C-P} =3.3 Hz), 133.2 (d, J_{C-P} =11.5 Hz), 120.0 (d, J_{C-P} = 199.7 Hz), 113.8 (d, J_{C-P} = 16.2 Hz), 61.7 (d, J_{C-P} = 5.7 Hz), 55.2, 16.1 (d, J_{C-P} = 6.9 Hz).

*(4-Methyl phenyl) phosphonic acid monoethyl ester (**1g**)*. A yellow oil; yield 750 mg (75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 11.40 (s, 1H), 7.68 (dd, J = 13.5, 7.7 Hz, 2H), 7.20 (dd, J = 8.0, 3.9 Hz, 2H), 4.06-3.99 (m, 2H), 2.35 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 142.5 (d, J_{C-P} = 3.2 Hz), 131.2 (d, J_{C-P} = 10.6 Hz), 128.9 (d, J_{C-P} = 15.6 Hz), 125.4 (d, J_{C-P} = 194.7 Hz), 61.7 (d, J_{C-P} = 5.6 Hz), 21.4, 16.1 (d, J_{C-P} = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 20.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_9H_{14}O_3P$: 201.0675; found: 201.0645.

*(4-tert-Butyl phenyl) phosphonic acid monoethyl ester (**1i**)*. A yellow oil; yield 872 mg (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 11.54 (s, 1H), 7.75 (s, 2H), 7.48-7.44 (m, 2H), 4.14-4.04 (m, 2H), 1.33-1.23 (m, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 155.6, 131.2 (d, J_{C-P} =10.6 Hz), 125.5 (d, J_{C-P} = 195.0 Hz), 125.3 (d, J_{C-P} = 15.5 Hz), 61.7 (d, J_{C-P} = 5.3 Hz), 34.9, 31.0, 16.1 (d, J_{C-P} = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 20.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{12}H_{20}O_3P$: 243.1145; found: 243.1115.

*(3,5-Dimethylphenyl) phosphonic acid monoethyl ester (**1l**)*. A yellow oil; yield 674 mg (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 12.19 (s, 1H), 7.42 (d, J = 14.0 Hz, 2H), 7.14 (s, 1H), 4.10-4.03 (m, 2H), 2.32 (s, 6H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 137.9 (d, J_{C-P} =16.0 Hz), 133.9 (d, J_{C-P} =3.4 Hz), 128.2 (d, J_{C-P} = 191.1 Hz), 128.8 (d, J_{C-P} = 10.0 Hz), 61.8 (d, J_{C-P} = 5.8 Hz), 21.1, 16.1 (d, J_{C-P} = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{10}H_{16}O_3P$: 215.0832; found: 215.0802.

*[4-(Trifluoromethyl)phenyl]phosphonic acid monoethyl ester (**1m**)*. A yellow oil; yield 851 mg (67 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 10.75 (s, 1H), 7.91 (dd, J = 13.4, 7.9 Hz, 2H), 7.68 (dd, J = 8.3, 3.5 Hz, 2H), 4.13-4.04 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 133.9-133.6 (m), 131.8 (d, J_{C-P} = 10.5 Hz), 125.3 -125.1 (m), 123.5 (d, J_{C-F} = 271.3 Hz), 62.5 (d, J_{C-P} = 5.9 Hz) , 16.1 (d, J_{C-P} = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 17.03. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_9H_{11}F_3O_3P$: 255.0392; found: 255.0388.

*[3-(Trifluoromethyl)phenyl]phosphonic acid monoethyl ester (**1o**)*. A yellow oil; yield 991 mg (78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 11.84 (s, 1H), 8.06 (d, J = 14.0 Hz, 1H), 7.98 (dd, J = 13.4, 7.7 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.57 (td, J = 7.8, 3.8 Hz, 1H), 4.13-4.05 (m, 2H), 1.30 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 134.6 (d, J_{C-P} = 10.0 Hz), 131.1-130.6 (m), 130.2 (d, J_{C-P} = 194.5 Hz), 128.9, 128.2-128.1 (m), 123.6 (d, J_{C-F} = 271.4 Hz), 62.5 (d, J_{C-P} = 5.9 Hz), 16.1 (d, J_{C-P} = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 16.70. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_9H_{11}F_3O_3P$: 255.0392; found: 255.0366.

General procedure for the synthesis of 3a-3x.

1a (0.2 mmol), **2a** (0.4 mmol), Acr^+-$MesClO_4^-$ (2.5 mg, 0.006 mmol), $[Co(dmgH)_2]PyCl$ (6.5 mg, 0.016 mmol) and CsF (46 mg, 0.3 mmol) were dissolved in $CHCl_3/H_2O$ (2 mL, *V/V* = 4:1). Then, the resulting mixture was degassed via 'freeze-pump-thaw' procedure (3 times) under argon atmosphere. After that, the solution was stirred at a distance of ~5 cm from a 6 W blue LEDs (450-460 nm) at ambient temperature for 24 h. Then another Acr^+-$MesClO_4^-$ (2.5 mg, 0.006 mmol) was added and stirred at under irradiation of 6 W blue LEDs until the reaction was completed, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 3:1) directly to give the desired product **3**.

*1,3,4-Triphenyl-1H-2,1-benzoxaphosphorin-1-oxide (**3a**)*(known compound). [5a] A light yellow solid; yield 56.80 mg (72%); mp 143 - 145 °C. IR (in KBr): 3132, 1489, 1245, 1122, 945, 731 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.97 - 7.91 (m, 2H), 7.62 - 7.56 (m, 2H), 7.54 - 7.49 (m, 2H), 7.43 (t, J = 7.8 Hz, 1H), 7.40 - 7.30 (m, 4H), 7.30 - 7.25 (m, 2H), 7.25 - 7.20 (m, 2H), 7.17 - 7.10 (m, 2H), 7.09 - 7.04 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.8 (d, J_{C-P} = 11.0 Hz), 138.6 (d, J_{C-P} = 5.3 Hz), 136.0, 134.6 (d, J_{C-P} = 5.1 Hz), 132.9 (d, J_{C-P} = 2.9 Hz), 132.4 (d, J_{C-P} = 2.5 Hz), 132.3 (d, J_{C-P} = 11.0 Hz), 131.5, 130.2 (d, J_{C-P} = 12.3 Hz), 129.9 (d, J_{C-P} = 144.3 Hz) , 129.1, 128.9, 128.6, 128.4 (d, J_{C-P} = 3.6 Hz), 127.8, 127.6, 127.5, 126.7 (d, J_{C-P} = 9.5 Hz), 123.1 (d, J_{C-P} =128.8 Hz), 119.1 (d, J_{C-P} = 11.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{20}O_2P$: 395.1195; found: 395.1182.

*6-Methyl-1-(4-methylphenyl)-3,4-diphenyl-1H-2,1-benzoxa-phosphorin 1-oxide (**3b**)*. A yellow solid; yield 41.40 mg (49%); mp 200 - 202 °C. IR (in KBr): 3138, 2975, 1601, 1480, 1236, 1121 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.88 - 7.78 (m, 2H), 7.44 - 7.31 (m, 7H), 7.28 - 7.25 (m, 2H) , 7.23 - 7.20 (m, 2H), 7.15 - 7.05 (m, 3H), 6.95 - 6.91 (dd, J = 8.3, 5.1 Hz, 1H), 2.44 (s, 3H), 2.31 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.2 (d, J_{C-P} = 11.0 Hz), 143.6 (d, J_{C-P} = 2.9 Hz), 137.8 (d, J_{C-P} = 22.9 Hz), 136.3, 136.0 (d, J_{C-P} = 5.3 Hz), 134.8 (d, J_{C-P} = 5.1 Hz), 133.3 (d, J_{C-P} = 11.0 Hz), 132.3 (d, J_{C-P} = 11.5 Hz), 131.6, 130.4 (d, J_{C-P} = 12.2 Hz), 130.0 (J_{C-P}= 101.2 Hz), 129.3 (d, J_{C-P} = 3.8 Hz), 129.0, 128.8, 128.2, 127.7, 127.5, 126.8 (d, J_{C-P} = 10.0 Hz), 123.2 (d, J_{C-P} = 128.2 Hz), 119.0 (d, J_{C-P} = 10.9 Hz), 21.7 (d, J = 1.4 Hz), 21.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{24}O_2P$: 423.1508; found: 423.1504.

*8-Methyl-1-(2-methylphenyl)-3,4-diphenyl-1H-2,1-benzoxa-phosphorin 1-oxide (**3c**)*(known compound). [5a] A white solid; yield 42.24 mg (50%); mp 125 - 127 °C. IR (in KBr): 3131, 2926, 1622, 1488, 1245, 1090 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.76 (dd, J = 15.6, 7.7 Hz, 1H), 7.64 - 7.61 (m, 1H), 7.42 - 7.23 (m, 3H), 7.20 - 7.09 (m, 6H), 7.07 - 7.03 (m, 4H), 6.86 (d, J = 7.6 Hz, 2H), 2.23 (s, 3H), 1.66 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.8 (d, J_{C-P} = 9.9 Hz), 142.5 (d, J_{C-P} =8.4 Hz), 138.3 (d, J_{C-P} = 2 Hz), 137.4 (d, J_{C-P} = 5.5 Hz), 137.1 (d, J_{C-P} =2.7 Hz), 136.9, 135.1 (d, J_{C-P} = 3.5 Hz), 133.4 (d, J_{C-P} = 14.8 Hz), 132.9 (d, J_{C-P} = 2.8 Hz), 131.5 (d, J_{C-P} = 12.0 Hz), 130.8, 129.8 (d, J_{C-P} = 186.1 Hz), 128.9, 128.3, 128.1 (d, J_{C-P} = 3.7 Hz), 128.0, 127.5, 127.2, 126.5 (d, J_{C-P} = 108.2 Hz), 125.0 (d, J_{C-P} = 15 Hz), 124.5, 123.0 (d, J_{C-P} = 12.8 Hz), 22.9 (d, J_{C-P} = 1.5 Hz), 20.8 (d, J_{C-P} = 4.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 31.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{24}O_2P$: 423.1508; found: 423.1516.

*6-tert-Butyl-1-(4-tertiary butylphenyl)-3,4-diphenyl-1H-2,1-benzoxa-phosphorin 1-oxide (**3d**)*. A white solid; yield 55.72 mg (55%); mp 104 - 105 °C. IR (in KBr): 3132, 2968, 1633, 1400, 1233, 1090 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.84 (dd, J = 12.9, 8.0 Hz, 2H), 7.65 (d, J = 14.8 Hz, 1H), 7.57-7.45 (m, 3H), 7.37 (d, J = 6.6 Hz, 4H), 7.22 (d, J = 7.7 Hz, 2H), 7.16 -7.05 (m, 4H), 6.97 (dd, J = 8.6, 5.4 Hz,1H), 1.35 (s, 9H), 1.26 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 156.4 (d, J_{C-P} = 2.9 Hz), 151.0 (d, J_{C-P} = 13.1 Hz), 146.4 (d, J_{C-P} = 11.0 Hz), 136.4, 136.3 (d, J_{C-P} = 5.6 Hz), 134.9 (d, J_{C-P} = 5.1 Hz), 131.9 (d, J_{C-P} = 11.4 Hz), 131.6, 129.9 (d, J_{C-P} = 2.6 Hz), 129.3 (d, J_{C-P} = 103.2 Hz), 129.0, 128.9, 128.3,128.0, 127.6 (d, J_{C-P} = 22.3 Hz), 127.5, 126.7 (d, J_{C-P} = 2.7 Hz), 125.6 (d, J_{C-P} = 13.7 Hz), 122.8 (d, J_{C-P} = 128.0 Hz), 118.9 (d, J_{C-P} = 10.7 Hz), 35.2, 34.8, 31.1 (d, J_{C-P} = 6.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{34}H_{36}O_2P$: 507.2447; found: 507.2442.

*6-Fluoro-1-(4-fluoro phenyl)-3,4-diphenyl-1H-2,1-benzoxa-phosphorin 1-oxide (**3e**)*. A white solid; yield 38.73 mg (45%); mp 175 - 177 °C. IR (in KBr): 3133, 2363, 1639, 1400, 1240, 1093, 949, 761 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.02 - 7.90 (m, 2H), 7.41 - 7.35 (m, 3H), 7.29 - 7.18 (m, 7H), 7.18 - 7.03 (m, 5H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 165.9 (dd, J_{C-F} = 253.7 Hz , J_{C-P} = 3.5 Hz), 161.4 (dd, J_{C-F} = 251.1 Hz , J_{C-P} = 19.8 Hz), 146.3 -146.2 (m), 135.1 (d, J_{C-P} = 21.7 Hz), 135.13,

135.10, 134.9 - 134.8 (m), 134.3 (d, J_{C-P} = 5.1 Hz), 131.4, 129.6 (dd, J_{C-F} = 11.2 Hz , J_{C-P} = 7.3 Hz), 129.01, 128.96, 128.6, 128.0, 127.6, 125.8-125.9 (m), 124.5 (dd, J_{C-F} = 19.2 Hz , J_{C-P} = 6.1 Hz), 120.0 (dd, J_{C-F} = 21.5 Hz , J_{C-P} = 2.7 Hz), 118.6 (d, J_{C-P} = 11.0 Hz), 116.6 -116.0 (m). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 21.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{18}F_2O_2P$: 431.1007; found: 431.1008.

*7-Trifluoromethyl -1-(3-trifluoromethyl phenyl)-3,4-diphenyl-1H-2,1-benzoxa- phosphorin 1-oxide (**3f**)*. A colorless oil; yield 33.94 mg (32 %); IR (in KBr): 3131, 2361, 1637, 1401, 1248, 1131, 958, 752.cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.24 (d, *J* = 13.5 Hz, 1H), 8.12 (dd, *J* = 13.0, 7.6 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.73 - 7.64 (m, 2H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 3.4 Hz, 3H), 7.34 (d, *J* = 4.1 Hz, 1H), 7.31 - 7.26 (m, 2H), 7.24 - 7.21 (m, 2H), 7.18 (d, *J* = 6.4 Hz, 1H), 7.16 - 7.09 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 148.2 (d, J_{C-P}=11.1 Hz), 139.6 (d, J_{C-P} = 5.8 Hz), 135.7 (d, J_{C-P} = 10.8 Hz), 134.7, 133.9 (d, J_{C-P} = 4.2 Hz), 131.6 (d, J_{C-P} = 6.0 Hz), 131.4 130.9 (d, J_{C-P} = 12.8 Hz), 129.8, 129.5, 129.4, 129.3, 129.1, 128.5, 127.8, 127.2 (d, J_{C-F} = 114.1 Hz), 125.9 (d, J_{C-P} = 128.7 Hz), 124.5, 124.3 - 124.2 (m), 124.1-124.0 (m), 123.8 - 123.6 (m), 122.1 (d, J_{C-P} = 2.3 Hz), 118.8 (d, J_{C-P} = 11.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 20.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{18}F_6O_2P$: 531.0943; found: 531.0916.

*5-Trifluoromethyl -1-(3-trifluoromethyl phenyl)-3,4-diphenyl-1H-2,1-benzoxa-phosphorin 1-oxide (**3f'**)*. A white solid; yield 38.19 mg (36 %); mp 211 - 213 ^{o}C. IR (in KBr): 3131, 2361, 1635, 1400, 1249, 1130, 968, 732.cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.16 (dd, *J* = 13.6, 8.8 Hz, 2H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.72 - 7.65 (m, 2H), 7.60 (t, *J* = 8.1 Hz, 1H), 7.42 (t, *J* = 3.4 Hz, 3H), 7.36 (dd, *J* = 8.3, 3.4 Hz, 1H), 7.32 - 7.27 (m, 2H), 7.18 (d, *J* = 7.6 Hz, 3H), 7.12 (d, *J* = 7.3 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.7 (d, J_{C-P} = 10.7 Hz), 141.3 (d, J_{C-P} = 3.2 Hz), 135.8 (d, J_{C-P} = 11.1 Hz), 135.7, 133.6 (d, J_{C-P} = 4.7 Hz), 132.4 (d, J_{C-P} = 2.1 Hz), 131.8 (d, J_{C-P} = 8.8 Hz), 131.5, 131.4 (d, J_{C-P} = 8.3 Hz), 130.9 (d, J_{C-P} = 32.7 Hz), 130.7 (d, J_{C-P} = 32.7 Hz), 129.7-129.6 (m), 129.3, 129.0, 128.9, 128.8, 128.7, 128.3, 127.7, 126.4-126.2 (m), 123.6 (dd, J_{C-F} = 279.4 Hz , J_{C-P} = 2.4 Hz), 123.2 (dd, J_{C-F} = 273.2 Hz , J_{C-P} = 4.1 Hz), 120.9 (d, J_{C-P} = 124.0 Hz), 119.5 (d, J_{C-P} = 11.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 19.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{18}F_6O_2P$: 531.0943; found: 531.0927.

*3,4-Diphenyl-1-ethoxy-6-methylbenz[c-1,2]oxaphosphinine 1-oxide (**3g**)*. A yellow oil; yield 41.40 mg (55%); IR (in KBr): 3131, 1633, 1401, 1161, 1040, 957, 757. cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.82-7.72 (m, 1H), 7.40 - 7.30 (m, 3H), 7.29 (s, 1H),7.24 - 7.10 (m, 7H), 6.85 (dd, *J* = 8.2, 6.6 Hz, 1H), 4.33 - 4.16 (m, 2H), 2.42 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm)= 147.0 (d, J_{C-P} = 9.0 Hz), 137.9 (d, J_{C-P} = 15.3 Hz), 137.6 (d, J_{C-P} = 6.8 Hz), 136.2, 134.6 (d, J_{C-P} = 5.7 Hz), 133.7 (d, J_{C-P} = 2.4 Hz), 131.5, 129.6 (d, J_{C-P} = 9.1 Hz), 128.9, 128.8, 128.4, 127.8, 127.6, 127.2 (d, J_{C-P} = 12.4 Hz), 120.7 (d, J_{C-P} = 170.0 Hz), 119.8 (d, J_{C-P} = 14 Hz), 62.9 (d, J_{C-P} = 6.7 Hz),

21.1, 16.5 (d, J = 6.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{22}O_3P$: 377.1301; found: 377.1294.

*3,4-Diphenyl-1-ethoxy-6-acetylbenz[c-1,2]oxaphosphinine 1-oxide (**3h**)*(known compound). [5a] A yellow oil; yield 43.67 mg (54%); IR (in KBr): 3132, 2926, 2362, 1686, 1401, 1290, 1180, 1026, 954, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.50 (dd, J = 15.5, 1.9 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.39 (s, 1H), 7.38 (d, J = 4.0 Hz, 2H), 7.30 - 7.23 (m, 4H), 7.24 - 7.14 (m, 3H), 7.07 (dd, J = 8.5, 6.1 Hz, 1H), 4.38 - 4.24 (m, 2H), 2.65 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 196.2, 149.9 (d, $J_{C\text{-}P}$ = 10.8 Hz), 144.2 (d, $J_{C\text{-}P}$ = 7.0 Hz), 135.6, 135.5 (d, $J_{C\text{-}P}$ = 1.6 Hz), 134.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 132.1, 131.4, 129.9 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.1, 128.9, 128.2, 127.8, 127.4 (d, $J_{C\text{-}P}$ = 10.2 Hz), 127.1, 121.1 (d, $J_{C\text{-}P}$ = 182.0 Hz), 119.6 (d, $J_{C\text{-}P}$ = 11.3 Hz), 63.4 (d, $J_{C\text{-}P}$ = 6.7 Hz), 26.6, 16.5 (d, $J_{C\text{-}P}$ = 5.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 9.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{22}O_4P$: 405.1250; found: 405.1245.

*3,4-Diphenyl-1-ethoxy-6- tert-butylbenz[c-1,2]oxaphosphinine 1-oxide (**3i**)*. A white solid; yield 35.15 mg (42%); mp 140 - 141 ^{o}C. IR (in KBr): 3132, 2362, 1634, 1478, 1401, 1268, 1169, 1052, 951, 752 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.96 (dd, J = 15.9, 2.2 Hz, 1H), 7.51 (dd, J = 8.3, 2.2 Hz, 1H), 7.40 - 7.30 (m, 3H), 7.28 - 7.08 (m, 7H), 6.90 (dd, J = 8.5, 6.8 Hz, 1H), 4.28 - 4.23 (m, 2H), 1.33 (d, J = 10.4 Hz, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.1 (d, $J_{C\text{-}P}$ = 14.6 Hz), 147.1 (d, $J_{C\text{-}P}$ = 10.8 Hz), 137.6 (d, $J_{C\text{-}P}$ = 6.9 Hz), 136.2 (d, $J_{C\text{-}P}$ = 1.5 Hz), 134.5 (d, $J_{C\text{-}P}$ = 5.7 Hz), 131.4, 130.2 (d, $J_{C\text{-}P}$ = 3.1 Hz), 128.8, 128.7, 128.4, 127.8, 127.6, 127.0 (d, $J_{C\text{-}P}$ = 12.9 Hz), 125.8 (d, $J_{C\text{-}P}$ = 2.4 Hz), 120.6 (d, $J_{C\text{-}P}$ = 152.6 Hz), 119.7 (d, $J_{C\text{-}P}$ = 11.7 Hz), 62.8 (d, $J_{C\text{-}P}$ = 7.0 Hz), 34.9, 31.1, 16.4 (d, $J_{C\text{-}P}$ = 6.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 11.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{28}O_3P$: 419.1771; found: 419.1771.

*3,4-Diphenyl-1-ethoxy-6- methoxybenz[c-1,2]oxaphosphinine 1-oxide (**3j**)* (known compound). [5b] A yellow solid; yield 24.32 mg (31%); mp 95 - 97 ^{o}C. IR (in KBr): 3131, 2361, 1631, 1401, 1236, 1150, 1063, 948, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.46 (d, J = 2.8 Hz, 1H), 7.42 (d, J = 2.8 Hz, 1H), 7.38 -7.30 (m, 3H), 7.21 (dd, J = 8.5, 4.0 Hz, 3H), 7.17 - 7.11 (m, 3H), 7.00 (dd, J = 8.9, 2.8 Hz, 1H), 6.89 (dd, J = 9.0, 7.2 Hz, 1H), 4.32 - 4.19 (m, 2H), 3.88 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 158.8 (d, $J_{C\text{-}P}$ = 19.0 Hz), 145.8 (d, $J_{C\text{-}P}$ = 10.6 Hz), 136.3, 134.5 (d, $J_{C\text{-}P}$ = 5.6 Hz), 133.1 (d, $J_{C\text{-}P}$ = 6.2 Hz), 131.4, 129.1(d, $J_{C\text{-}P}$ = 14.3 Hz), 128.8, 128.7, 128.2, 128.0 (d, $J_{C\text{-}P}$ = 42.2 Hz), 127.6, 122.0 (d, $J_{C\text{-}P}$ = 179.6 Hz), 120.1 (d, $J_{C\text{-}P}$ = 3.0 Hz), 119.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 112.5 (d, $J_{C\text{-}P}$ = 10.2 Hz), 63.0 (d, $J_{C\text{-}P}$= 6.6 Hz), 55.7, 16.4 (d, $J_{C\text{-}P}$ = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{22}O_4P$: 393.1250; found: 393.1253.

*3,4-Diphenyl-1-ethoxy-6-fluorobenz[c-1,2]oxaphosphinine 1-oxide (**3k**)* (known compound).[5b] A yellow oil; yield 26.62 mg (35%); IR (in KBr): 3132, 2362, 1634, 1477, 1401, 1083, 958, 785 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.66 - 7.60 (m, 1H), 7.37 - 7.35 (m, 3H), 7.25 - 7.10 (m, 8H), 6.99 - 6.94 (m, 1H), 4.36 - 4.18 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 162.6 (d, J_{C-P} = 21.7 Hz), 160.1 (d, J_{C-P} = 21.7 Hz), 147.1 (d, J_{C-P} = 3.1 Hz), 136.5 (dd, J_{C-P} = 5.9 Hz , J_{C-F} = 2.8 Hz), 135.8, 134.2 (d, J_{C-P} = 5.9 Hz), 131.4, 129.8 (dd, J_{C-P} = 14.0 Hz , J_{C-F} = 7.3 Hz), 129.0, 128.7, 128.6, 128.0, 127.7, 120.2 (dd, J_{C-F} = 20.7 Hz , J_{C-P} = 2.1 Hz), 118.2 (J_{C-P} = 211.6 Hz), 115.8 (dd, J_{C-F} = 22.8 Hz , J_{C-P} = 9.2 Hz), 63.3 (d, J_{C-P} = 6.3 Hz), 16.4 (d, J_{C-P} = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{19}FO_3P$: 381.1050; found: 381.1051.

*3,4-Diphenyl-1-ethoxy-5-methyl-7-methylbenz[c-1,2]-oxaphosphinine 1-oxide (**3l**)*. A white solid; yield 49.19 mg (63%); mp 128 -130 °C. IR (in KBr): 3133, 2989, 1401, 1256, 1027, 961, 767 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.40 - 7.29 (m, 3H), 7.20 (dd, J = 7.0, 3.3 Hz, 3H), 7.16 - 7.09 (m, 4H), 7.04 (d, J = 4.3 Hz, 1H), 6.58 (d, J = 5.7 Hz, 1H), 4.33 - 4.14 (m, 2H), 2.73 (d, J = 1.8 Hz, 3H), 2.21 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 147.2 (d, J_{C-P} = 10.4 Hz), 142.9 (d, J_{C-P} = 2.3 Hz), 141.1 (d, J_{C-P} = 9.9 Hz), 141.08, 136.6, 134.6 (d, J_{C-P} = 5.8 Hz), 131.6, 131.1, 130.9, 128.8, 128.3, 127.7, 127.5, 125.7 (d, J_{C-P} = 12.3 Hz), 119.4 (d, J_{C-P} = 11.5 Hz), 116.4 (d, J_{C-P} = 178.6 Hz), 62.6 (d, J_{C-P} = 6.9 Hz), 21.7, 21.4, 16.4 (d, J_{C-P} = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{24}O_3P$: 391.1458; found: 391.1463.

*3,4-Diphenyl-1-ethoxy-6-trifluoromethylbenz[c-1,2]oxaphosphinine 1-oxide (**3m**)*. A yellow oil; yield 71.43 mg (83%); IR (in KBr): 3131, 1601, 1488, 1271, 1241, 1026, 955, 756 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.20 (dd, J = 15.3, 2.0 Hz, 1H), 7.68 (d, J = 8.5 Hz, 1H), 7.44 - 7.32 (m, 3H), 7.29 - 7.13 (m, 7H), 7.09 (dd, J = 8.5, 6.0 Hz, 1H), 4.41- 4.22 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm)= 149.7 (d, J_{C-P} = 10.3 Hz), 143.4 (d, J_{C-P} = 7.0 Hz), 135.4, 133.9 (d, J_{C-P} = 5.7 Hz), 129.7, 129.6, 129.3, 129.1 (d, J_{C-P} = 9.8 Hz), 128.9, 128.3, 127.8, 127.6. 127.5, 126.5 - 126.6 (m), 124.8, 121.6 (d, J_{C-F} = 182.8 Hz), 119.3 (d, J_{C-P} = 11.4 Hz), 63.5 (d, J_{C-P} = 6.6 Hz), 16.5 (d, J_{C-P} = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{19}F_3O_3P$: 431.1018; found: 431.1019.

*3,4-Diphenyl-1-ethoxybenz[c-1,2]oxaphosphinine 1-oxide (**3n**)* (known compound). [5a] A yellow solid; yield 34.06 mg (47%); mp 124 -126 °C. IR (in KBr): 3132, 1606, 1467, 1441, 1269, 1025, 950, 761 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.98 - 7.92 (m, 1H), 7.50 - 7.41 (m, 2H), 7.39 - 7.31 (m, 3H), 7.30 - 7.09 (m, 7H), 7.02 - 6.93 (m, 1H), 4.39 - 4.15 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 147.8 (d, J_{C-P} = 10.3 Hz), 140.1 (d, J_{C-P} = 6.8 Hz), 136.0 (d, J_{C-P} = 1.2 Hz), 134.4 (d, J_{C-P} = 5.5 Hz), 132.8 (d, J_{C-P} = 2.5 Hz), 131.5, 129.3 (d, J_{C-P} = 8.9 Hz), 128.8, 128.7, 128.5,

127.8, 127.6, 127.5, 127.1 (d, J_{C-P} = 12 Hz), 120.8 (d, J_{C-P} = 180.5 Hz), 119.8 (d, J_{C-P} = 11.8 Hz), 63.0 (d, J_{C-P} = 6.6 Hz), 16.4 (d, J_{C-P} = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 10.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{20}O_3P$: 363.1145; found: 363.1146.

*3,4-Diphenyl-1-ethoxy-7-trifluoromethylbenz[c-1,2]oxaphosphinine 1-oxide (**3o**)*. A white solid; yield 29.26 mg (34%); mp 124 -127 °C. IR (in KBr): 3130, 1634, 1401, 1265, 1237, 1033, 973, 696 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) = 8.07 (dd, *J* = 14.6, 7.9 Hz, 1H), 7.67 (dd, *J* = 7.7, 2.4 Hz, 1H), 7.45 - 7.30 (m, 3H), 7.28 - 7.09 (m, 8H), 4.35 - 4.25 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.2 (d, J_{C-P} = 10.5 Hz), 141.1 (d, J_{C-P} = 7.0 Hz), 135.0, 134.0 (d, J_{C-P} = 5.6 Hz), 131.3, 130.1, 130.0, 129.2, 129.0, 128.8, 128.4, 127.8, 125.0 (d, J_{C-F} = 73.4 Hz), 124.1-123.9 (m), 123.8 -123.5 (m), 121.9, 119.3 (d, J = 11.6 Hz), 63.5 (d, J_{C-P} = 6.6 Hz), 16.5 (d, J_{C-P} = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 8.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{19}F_3O_3P$: 431.1018; found: 431.1021.

*3,4-Diphenyl-1-ethoxy-5-trifluoromethylbenz[c-1,2]oxaphosphinine 1-oxide (**3o'**)*. A white solid; yield 24.09 mg (28%); mp 179 -180 °C. IR (in KBr): 3132, 1621, 1400, 1267, 1214, 1020, 971, 757 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.74 (dd, *J* = 7.8, 4.8 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.39 -7.35 (m, 3H), 7.25 -7.14 (m, 8H), 4.47- 4.33 (m, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 148.0 (d, J_{C-P} = 10.3 Hz), 142.5 (d, J = 4.5 Hz), 135.9, 133.8 (d, J_{C-P} = 5.5 Hz), 132.0, 131.5, 131.2 (d, J_{C-P} = 10.3 Hz), 129.1, 128.9, 128.7, 128.2, 127.7, 125.8-125.6 (m), 123.3 (dd, J_{C-F} = 272.9 Hz, J_{C-P} = 5.6 Hz), 120.8, 119.7 (d, J_{C-P} = 12.0 Hz), 119.0, 63.9 (d, J_{C-P} = 6.9 Hz), 16.3 (d, J_{C-P} = 6.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 5.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{19}F_3O_3P$: 431.1018; found: 431.1020.

*3,4-Bis(4-tert-butylphenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide (**3p**)*. A white solid; yield 71.94 mg (71%); mp 113 - 115 °C. IR (in KBr): 3130, 2961, 1608, 1244, 1060, 744 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.00 - 7.89 (m, 2H), 7.63 - 7.57 (m, 2H), 7.51 (m, *J* = 7.6, 3.7 Hz, 2H), 7.43 (dd, *J* = 16.0, 8.0 Hz, 3H), 7.31 (dd, *J* = 7.5, 2.9 Hz, 1H), 7.23- 7.18 (m, 2H), 7.19 - 7.12 (m, 2H), 7.13 - 7.05 (m, 3H), 1.37 (s, 9H), 1.22 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.2 (d, J_{C-P} = 57.7 Hz), 146.8 (d, J_{C-P} = 11.0 Hz), 139.1 (d, J_{C-P} = 5.3 Hz), 133.1, 132.7 (d, J_{C-P} = 2.7 Hz), 132.4, 132.3, 131.8 (d, J_{C-P} = 5.2 Hz), 131.2, 130.3 (d, J_{C-P} = 144.2 Hz), 130.2 (d, J_{C-P} = 12.2 Hz), 128.7, 128.6, 128, 127.3 (d, J_{C-P} = 14.3 Hz), 126.9 (d, J_{C-P} = 9.5 Hz), 125.8, 124.4, 123.0 (d, J_{C-P} = 128.8 Hz), 118.5 (d, J_{C-P} = 10.8 Hz), 34.7, 34.5, 31.4, 31.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{34}H_{36}O_2P$: 507.2447; found: 507.2442.

*3,4-Bis(3,5-dimethylphenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide (**3q**)*. a white solid; yield 62.17 mg (69%); mp 80 - 81 °C. IR (in KBr): 3131, 2917, 2361, 1598, 1401, 1244, 1123, 905, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.97 - 7.87 (m, 2H), 7.65 - 7.57 (m, 2H), 7.56 - 7.39 (m, 4H), 7.29 (s, 1H), 7.07 (dd, *J* = 8.2, 4.7 Hz, 1H), 7.00 (s, 1H), 6.90 (d, *J* = 10.7 Hz, 4H), 2.30 (s, 6H), 2.11 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) *δ* (ppm) = 146.8 (d, J_{C-P} = 11.1 Hz), 139.1 (d, J_{C-P} = 5.4 Hz), 136.7, 135.9, 134.4 (d, J_{C-P} = 7.0 Hz), 132.8 (d, J_{C-P} = 2.9 Hz), 132.4 (d, J_{C-P} = 2.6 Hz), 132.3, 132.2, 131.0, 130.2, 130.1 (d, J_{C-P} = 2.7 Hz), 129.6, 129.2 (d, J_{C-P} = 3.3 Hz), 128.5 (d, J_{C-P} = 13.9 Hz), 127.3 (d, J_{C-P} = 14.3 Hz), 127.0, 126.9, 123.0 (d, J_{C-P} = 128.8 Hz), 118.9 (d, J_{C-P} = 10.8 Hz), 21.2, 21.1. ^{31}P NMR (162 MHz, $CDCl_3$): *δ* = 24.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{28}O_2P$: 451.1821; found: 451.1806.

*3,4-Bis(4-methylphenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide (**3r**)* (known compound).[5a] A yellow solid; yield 48.16 mg (57%); mp 222 - 224 °C. IR (in KBr): 3139, 2363, 1639, 1401, 1237, 1057, 944, 739 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 7.92 (dd, *J* = 13.2, 7.7 Hz, 2H), 7.65 - 7.55 (m, 2H), 7.54 - 7.46 (m, 2H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 6.8 Hz, 1H), 7.23 - 7.11 (m, 6H), 7.09 - 7.01 (m, 1H), 6.90 (t, *J* = 11.5 Hz, 2H), 2.38 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) *δ* (ppm) = 146.9 (d, J_{C-P} = 11.0 Hz), 139.0 (d, J_{C-P} = 5.2 Hz), 138.4, 137.4, 133.1, 132.9 (d, J_{C-P} = 2.6 Hz), 132.4 (d, J_{C-P} = 2.6 Hz), 132.3 (d, J_{C-P} = 5.2 Hz), 131.9 (d, J_{C-P} = 5.2 Hz), 131.4, 131.0, 130.2 (d, J_{C-P} = 12.3 Hz), 129.7, 129.5 (d, J_{C-P} = 13.4 Hz), 128.6 (d, J_{C-P} = 69.5 Hz), 128.5 (d, J_{C-P} = 13.9 Hz), 127.3 (d, J_{C-P} = 14.2 Hz), 126.7 (d, J_{C-P} = 9.5 Hz), 123.0 (d, J_{C-P} = 128.7 Hz), 118.4 (d, J_{C-P} = 11.0 Hz), 21.3, 21.2. ^{31}P NMR (162 MHz, $CDCl_3$): *δ* = 24.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{24}O_2P$: 423.1508; found: 423.1510.

*3,4-Bis(2-methylphenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide (**3s**)*. A white solid; yield 67.59 mg (80%); mp 76 - 77 °C. IR (in KBr): 3146, 2974, 2360, 1627, 1401, 1063, 948, 756 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* (ppm) = 7.96 - 7.83 (m, 2H), 7.59 - 7.52 (m, 2H), 7.55 - 7.47 (m, 2H), 7.48 - 7.36 (m, 2H), 7.15 (d, *J* = 6.0 Hz, 2H), 7.10 - 7.03 (m, 5H), 6.95 - 6.78 (m, 2H), 2.40 (s, 3H), 2.17 (s, 1.7 H), 2.11 (s, 1.3 H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) *δ* (ppm) = 148.5 (d, J_{C-P} = 11.2 Hz), 148.3 (d, J_{C-P} = 11.1 Hz), 137.9, 137.3, 137.7 (d, J_{C-P} = 5.2 Hz), 137.0 (d, J_{C-P} = 4.5 Hz), 134.8 (d, J_{C-P} = 15.7 Hz), 134.2 (d, J_{C-P} = 4.5 Hz), 133.0 (d, J_{C-P} = 3.0 Hz), 132.8, 132.6, 132.5, 131.9 (d, J_{C-P} = 11.3 Hz), 131.4, 131.3, 130.5 (d, J_{C-P} = 11.6 Hz), 130.4 (d, J_{C-P} = 10.1 Hz), 130.1, 130.0, 130.0, 129.4 (d, J_{C-P} = 88.1 Hz), 129.4, 128.8, 128.5, 128.4, 128.0, 125.6, 124.9 (d, J_{C-P} = 3.6 Hz), 123.2 (d, J_{C-P} = 128.5 Hz), 122.5 (d, J_{C-P} = 127.2 Hz), 119.3 (d, J_{C-P} = 11.3 Hz), 118.4 (d, J_{C-P} = 10.7 Hz), 29.7, 20.0 (d, J_{C-P} = 4.3 Hz), 19.8. ^{31}P NMR (162 MHz, $CDCl_3$): *δ* = 25.3, 24.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{24}O_2P$: 423.1508; found: 423.1509.

*3,4-Bis(4-fluorophenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide (**3t**)*. A white solid; yield 60.25 mg (70%); mp 167 - 168 °C. IR (in KBr): 3133, 1619, 1507, 1401, 1226, 1059, 950, 743 cm^{-1}. ^{1}H NMR

(400 MHz, $CDCl_3$) δ (ppm) = 7.93 (dd, J = 13.4, 7.5 Hz, 2H), 7.68 - 7.58 (m, 1H), 7.57 - 7.51 (m, 3H), 7.47 (t, J = 7.8 Hz, 1H), 7.36 (dd, J = 7.5, 2.8 Hz, 1H), 7.25 - 7.19 (m, 4H), 7.10 (t, J = 8.4 Hz, 2H), 7.03 (dd, J = 8.2, 4.8 Hz, 1H), 6.83 (t, J = 8.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 162.4 (d, J_{C-F} = 248.6 Hz), 161.3 (d, J_{C-F} = 246.7 Hz), 146.2 (d, J_{C-P} = 10.8 Hz), 133.3, 133.2, 133.1 (d, J_{C-P} = 2.8 Hz), 132.6 (d, J_{C-P} = 2.5 Hz), 132.5, 132.3, 131.8 (d, J_{C-P} = 3.7 Hz), 131.1 (d, J_{C-P} = 8.3 Hz), 130.4, 130.3, 128.6 (d, J_{C-P} = 14.0 Hz), 127.8 (d, J_{C-P} = 14.5 Hz), 126.5 (d, J_{C-P} = 9.8 Hz), 123.2 (d, J_{C-P} = 128.9 Hz), 118.2 (d, J_{C-P} = 12.2 Hz), 116.1 (d, J_{C-F} = 21.1 Hz), 114.8 (d, J_{C-F} = 21.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{18}F_2O_2P$: 431.1007; found: 431.1004.

*3,4-Bis(4-chlorophenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide (**3u**)* (known compound).[5a] A white solid; yield 56.52 mg (61%); mp 90 - 93 °C. IR (in KBr): 3131, 1589, 1487, 1400, 1236, 1090, 948, 748 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.97 - 7.86 (m, 2H), 7.67 - 7.50 (m, 4H), 7.47 (t, J = 7.7 Hz, 1H), 7.46 - 7.38 (m, 3H), 7.21 (d, J = 7.9 Hz, 2H), 7.18 - 7.09 (m, 4H), 7.01 (dd, J = 8.2, 4.9 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.0 (d, J_{C-P} = 10.9 Hz), 137.9 (d, J_{C-P} = 5.1 Hz), 134.7, 134.2 (d, J_{C-P} = 6.5 Hz), 133.2 (d, J_{C-P} = 2.9 Hz), 133.0, 132.9, 132.6 (d, J_{C-P} = 2.5 Hz), 132.4 (d, J_{C-P} = 11.1 Hz), 130.5, 130.3, 130.1, 129.4, 128.7 (d, J_{C-P} = 14.0 Hz), 128.6, 128.0, 127.9 (d, J_{C-P} = 14.3 Hz), 126.6 (d, J_{C-P} = 9.5 Hz), 123.2 (d, J_{C-P} = 128.9 Hz), 118.5 (d, J_{C-P} = 11.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{18}Cl_2O_2P$: 463.0416; found: 463.0430.

*3,4-Bis(4-bromophenyl)-1-phenyl-1H-2,1-benzoxaphosphorin 1-oxide (**3v**)* (known compound).[5a] A white solid; yield 27.61 mg (25%); mp 193 - 194 °C. IR (in KBr): 3132, 1633, 1400, 1239, 1072, 947, 746 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.89 - 7.79 (m, 2H), 7.60 - 7.50 (m, 1H), 7.47 (dd, J = 6.1, 4.1 Hz, 5H), 7.40 (t, J = 8.2 Hz, 1H), 7.33 - 7.27 (m, 1H), 7.23 - 7.17 (m, 2H), 7.08 (d, J = 7.9 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.94 (dd, J = 8.1, 4.8 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 146.0 (d, J_{C-P} = 10.8 Hz), 137.9 (d, J_{C-P} = 5.1 Hz), 134.7, 133.4 (d, J_{C-P} = 5.1 Hz), 133.2, 133.1, 132.7 (d, J_{C-P} = 2.4 Hz), 132.5, 132.4, 132.3, 131.0, 130.4 (d, J_{C-P} = 12.4 Hz), 130.2, 128.6 (d, J_{C-P} = 14.1 Hz), 128.0 (d, J_{C-P} = 14.4 Hz), 126.6 (d, J_{C-P} = 9.4 Hz), 123.2 (d, J_{C-P} = 128.8 Hz), 123.1, 122.3, 118.6 (d, J_{C-P} = 11.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{26}H_{18}Br_2O_2P$: 550.9406; found: 550.9408.

According to the general procedure, the mixture of **3w** and **3w'** were obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 3/1) as a white solid, yield 64.3 mg (75%). The ratio of the isomers were determined based on the intergration of the character peak located at 2.40 ppm (H-1 of 3w) and 2.25 ppm (H-1'of 3w') and by ^{31}P NMR, the ratio of isomers (**3w**/**3w'**) is

3:1.4. The mixture of **3w** and **3w'**: IR (in KBr): 3130, 2361, 1637, 1506, 1400, 952, 750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.96 - 7.90 (m, 2H), 7.65 - 7.51 (m, 4H), 7.48 - 7.42 (m, 1H), 7.35 - 7.31 (m, 1H), 7.25 -7.19 (m, 3H), 7.16 – 6.99 (m, 4H), 6.94 (d, J = 8.1 Hz, 1H), 6.81 (t, J = 8.7 Hz, 1H), 2.41 (s, 2.05 H), 2.25 (s, 0.95 H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 162.4 (d, $J_{C\text{-}F}$ = 248.3 Hz), 145.8 (d, $J_{C\text{-}P}$ = 10.7 Hz), 138.8-138.7 (m), 137.8, 133.4 (d, $J_{C\text{-}P}$ = 7.7 Hz), 133.1(d, $J_{C\text{-}P}$ = 2.8 Hz), 132.8, 132.5, 132.5, 132.5, 132.4, 132.4, 132.3, 131.4, 131.1 (d, $J_{C\text{-}P}$ = 8.3 Hz), 130.3, 130.2, 129.8, 129.0, 128.7, 128.5, 128.4, 127.8 (d, $J_{C\text{-}F}$ = 9.6 Hz), 126.9 (d, $J_{C\text{-}F}$ = 9.6 Hz), 123.1 (d, $J_{C\text{-}P}$ = 129.0 Hz), 114.7 (d, $J_{C\text{-}P}$ = 21.6 Hz), 21.3, 21.2. MP 76 - 78 °C. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.5, 24.4 (3:1.4). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{21}FO_2P$: 427.1258; found: 427.1245.

According to the general procedure, the mixture of **3x** and **3x'** were obtained by column chromatography with the eluting (petroleum ether/ethyl acetate = 3/1) as a white solid, yield 45.2 mg (47%). The ratio of the isomers were determined based on the intergration of the character peak located at 2.40 ppm (H-1 of **3x**) and 2.25 ppm (H-1' of **3x'**) and by ^{31}P NMR. The ratio of isomers (**3x**/**3x**') is 3:1.3. The pure isomer **3x** was isolated further by HPLC. **3x**: mp 77 - 78 °C. IR (in KBr): 3478, 3234, 3133, 2027, 1638, 1617, 1469, 1401, 1242, 949, 742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.98 - 7.89 (m, 2H), 7.62 (d, J = 1.6 Hz, 2H), 7.56 - 7.52 (m, 2H), 7.47 (t, J = 8.0 Hz, 1H), 7.36 (s, 5H), 7.22 (d, J = 7.7 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 7.09 (dd, J = 8.2, 4.8 Hz, 1H), 2.42 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) = 144.9 (d, $J_{C\text{-}P}$ = 10.7 Hz), 138.4 (d, $J_{C\text{-}P}$ = 5.2 Hz), 138.1, 133.2 (d, $J_{C\text{-}P}$ = 3.0 Hz), 132.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.4, 132.3, 132.2, 131.2, 130.2 (d, $J_{C\text{-}P}$ = 12.4 Hz), 130.1 (d, $J_{C\text{-}P}$ =19.1 Hz), 130.0-129.8 (m), 129.3, 128.8 (d, $J_{C\text{-}P}$ = 14.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 13.9 Hz), 128.0 (d, $J_{C\text{-}P}$ = 14.5 Hz), 127.1 (d, $J_{C\text{-}P}$ = 9.5 Hz), 123.8 (d, $J_{C\text{-}P}$ = 170.8 Hz), 124.5 - 124.4 (m), 123.4 (d, $J_{C\text{-}F}$ = 129.1 Hz), 120.5 (d, $J_{C\text{-}P}$ = 11.0 Hz), 21.3. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 24.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{21}F_3O_2P$: 477.1226; found: 477.1201.

Acknowledgment: We are grateful to the National Natural Science Foundation of China (NOs. 21472057, 21772053) and Program of Introducing Talents of Discipline to Universities of China (111 Program, B17019) and the Open Project of Key Laboratory of Theoretical Chemistry & Molecular Simulation of Ministry of Education, Hunan University of Science and Technology (LKF104) for the financial support of this research.

Supporting Information Available Full experimental details, spectroscopic data of **3**, CIF file for **3a, 3w** and **3x**. This material is available free of charge via the Internet at http://pubs.acs.org.

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