JOC The Journal of Organic Chemistry

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Palladium-Catalyzed Domino Addition and Cyclization of Arylboronic Acids with 3-Hydroxyprop-1-yn-1-yl Phosphonates Leading to 1,2-Oxaphospholenes

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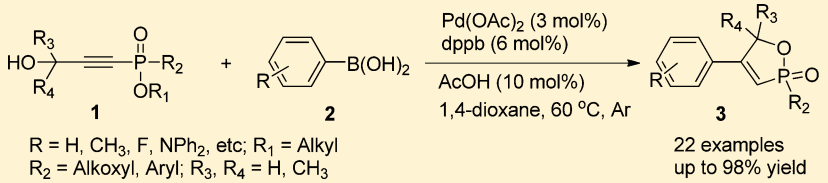
Supporting Information



ABSTRACT: A novel and efficient palladium-catalyzed domino addition−cyclization of a wide range of arylboronic acids with various 3-hydroxyprop-1-yn-1-yl phosphonates has been developed, affording a convenient and powerful tool for the preparation of valuable 1,2-oxaphospholenes with mild reaction conditions, broad substrate applicability, and good to excellent yields. Mechanistic studies revealed that the reaction might involve Michael addition and nucleophilic substitution.

Phosphorus-containing heterocycles have attracted significant attention to synthetic chemists over the past several decades due to their unusual structural features and their association with diverse biological activities and unique properties.[1] Among them, 1,2-oxaphosphole-3-ene 2-oxide derivatives have received considerable interests owing to their wide-ranging biological properties such as antimicrobial activity,[2] cytotoxicity and genotoxicity,[3] and antiviral activity.[4] In addition, 1,2-oxaphosphole-3-ene 2-oxides are also an important class of versatile precursors for the preparation of various valuable organophosphorous derivatives,[5] especially for 1,2-oxaphospholane 2-oxides through an addition or reduction reaction (Scheme 1), which exhibit numerous interesting biological activities as carbohydrate mimics.[6] However, there have been only a few reports of the synthesis of 1,2-oxaphosphole-3-ene 2-oxides.[7] In 2001 and 2003, Lee reported two protocols for the preparation of 1,2-oxaphosphole-3-ene 2-oxides through using complicated 2-organyltelluro-1-alkenl-phosphonate and an air-sensitive Grignard reagent in a two-step process[7f] or treatment of α-acylallylphosphonates which were difficult to obtain with *m*-CPBA in the presence of $MgSO_4$.[5] In 2007, Ma and co-workers developed a cyclization−Heck reaction of monoesters of 1,2-allenyl phosphonic acids with alkenes leading to 1,2-oxaphosphole-3-ene 2-oxide derivatives.[7g] Despite their usefulness, almost all of these methods have common problems such as uncommon reactants, excess reagents, poor substrate scope, relatively strict reaction conditions, multistep reactions, or lower yields, thus increasing the cost and limiting their applications. As part of our ongoing endeavors to develop the new methods for the synthesis of organic phosphorus compounds,[8] we herein revealed the first example of a single-step preparation of valuable 1,2-oxaphosphole-3-ene 2-oxides through a facile and efficient Pd-catalyzed domino addition−cyclization reaction of various readily available arylboronic acids with 3-hydroxyprop-1-yn-1-yl phosphonates, which could be conveniently prepared by using our recently reported method,[9] with broad substrate applicability, mild reaction conditions, and good to excellent yields.

Scheme 1. Structure of 1,2-Oxaphospholene and 1,2-Oxaphospholane 2-Oxide

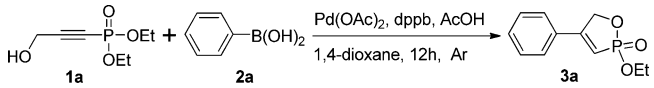
1,2-oxaphosphole-3-ene 2-oxide 1,2-oxaphospholane 2-oxide

Initially, to investigate the feasibility of the present reaction, diethyl (3-hydroxyprop-1-yn-1-yl)phosphonate **1a** and phenylboronic acid **2a** were chosen as model substrates in the presence of 3 mol % $Pd(OAc)_2$ catalyst, 10 mol % AcOH in 1.0 mL of 1,4-dioxane under argon. A screening of the ligands illustrated that dppb was the best choice for this reaction

Received: May 5, 2015
Published: June 11, 2015

DOI: 10.1021/acs.joc.5b00999
J. Org. Chem. 2015, 80, 6908−6914

Table 1. Optimization of Reaction Conditions[a]



1a 2a 3a

entry	catalyst	ligand	acid	solvent	temp (°C)	yield (%)
1	$Pd(OAc)_2$	2,2′-bpy	AcOH	1,4-dioxane	50	0
2	$Pd(OAc)_2$	TMEDA	AcOH	1,4-dioxane	50	trace
3	$Pd(OAc)_2$	dppe	AcOH	1,4-dioxane	50	3
4	$Pd(OAc)_2$	dppp	AcOH	1,4-dioxane	50	21
5	$Pd(OAc)_2$	dppb	AcOH	1,4-dioxane	50	45
6	**$Pd(OAc)_2$**	**dppb**	**AcOH**	**1,4-dioxane**	**60**	**98**
7	$Pd(OAc)_2$	dppb	AcOH	1,4-dioxane	70	80
8	$PdCl_2$	dppb	AcOH	1,4-dioxane	60	0
9	$Pd(PPh_3)_4$	dppb	AcOH	1,4-dioxane	60	90
10	$Pd(OAc)_2$	dppb	AcOH	CH_3CN	60	0
11	$Pd(OAc)_2$	dppb	AcOH	THF	60	61
12	$Pd(OAc)_2$	dppb	AcOH	toluene	60	55
13	$Pd(OAc)_2$	dppb	AcOH	DMF	60	11
14	$Pd(OAc)_2$	dppb	TfOH	1,4-dioxane	60	9
15	$Pd(OAc)_2$	dppb	PivOH	1,4-dioxane	60	80
16	–	dppb	AcOH	1,4-dioxane	60	0
17	$Pd(OAc)_2$	–	AcOH	1,4-dioxane	60	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), acid (10 mol %), catalyst (3 mol %), ligand (6 mol %), solvent (1.0 mL), 12 h, under Ar.

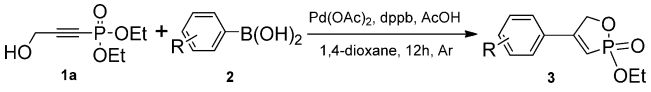
(Table 1, entries 1−5), affording the desired product **3a** in 45% yield (Table 1, entry 5). Encouraged by the promising result, the effect of temperature was further examined and the results showed that increasing the temperature to 60 °C could greatly improve the yield up to 98%; however, continuously increasing the temperature to 70 °C led to the yield decrease (Table 1, entries 6 and 7). Subsequently, some other palladium catalysts including $PdCl_2$ and $Pd(PPh_3)_4$ were also evaluated, but no better results were obtained (Table 1, entries 8 and 9). In addition, different solvents such as CH_3CN, THF, toluene, and DMF were evaluated, only providing **3a** in 0−61% yields (Table 1, entries 10−13). Some other acids such as TfOH and PivOH were applied in this reaction, but only produced **3a** in yields of 9% and 80%, respectively (Table 1, entries 14 and 15). Without $Pd(OAc)_2$ or dppb, the domino reaction could not perform under the optimal reaction conditions (Table 1, entries 16 and 17). With the optimized reaction conditions in hand, the scope of this domino reaction was surveyed (Table 2 and 3). As shown in Table 2, the arylboronic acids bearing various functional groups all worked well under the present conditions to afford the desired 1,2-oxaphosphole-2-oxide derivatives with good to excellent yields, demonstrating that this method is a simple and practical tool for the synthesis of various valuable oxaphospholenes. Thus, many functional groups including methyl, *n*-butyl, 3,4-OCH_2O, naphthyl, diphenylamino, fluoro, carbonyl, and hydroxyl were all tolerated. Substituted phenylboronic acids with electron-donating methyl, *n*-butyl, and 3,4-methylenedioxy groups reacted smoothly with **1a** to provide products **3b**−**3d** in excellent yield (Table 2, entries 2−4). 2-Naphthylboronic acid **2e** and 4-(diphenylamino)phenylboronic acid **2f** also efficiently reacted in high yield (**3e**, **3f**, 76%, 78%, respectively, Table 2, entries 5 and 6). Some electron-deficient arylboronic acids **2g**−**2i** could provide the corresponding products **3g**−**3i** in moderate to good yields at a higher temperature of 70 °C (Table 2, entries 7−9). Notably, carbonyl group substituted substrates **2h** and **2i** containing a reactive aldehyde or ketone unit could also be compatible with the present protocol, giving the desired products **3h** and **3i** selectively in a moderate yield without needing any protection of the aldehyde or ketone group. Furthermore, (4-(hydroxymethyl)phenyl)boronic acid **2j** containing a reactive hydroxyl group could also be used in this domino reaction to produce **3j** in 52% yield (Table 2, entry 10).

The versatility of the reaction was further investigated for the domino reaction of different (3-hydroxyprop-1-yn-1-yl)-phosphonate substrates with several phenylboronic acid derivatives to afford the corresponding products in moderate to excellent yields. In regard to phosphorus-containing substrate **1**, in addition to **1a**, ethyl (3-hydroxyprop-1-yn-1-yl)(phenyl)phosphinate **1b**, diisopropyl (3-hydroxyprop-1-yn-1-yl)phosphonate **1c**, and dimethyl (3-hydroxyprop-1-yn-1-yl)phosphonate **1d** were all suitable reaction partners for this domino reaction, generating desired products **3k**−**3t** in 47−98% yields (Table 3, entries 1−10). In contrast to **1a**, **1b**, and **1d**, **1c** afforded a lower yield under similar reaction conditions (Table 3, entries 7−9), probably due to the higher stability of the diisopropyl group adjacent to the phosphorus atom, which blocked the intramolecular nucleophilic substitution reaction. Moreover, we also investigated the steric-hindrance effect of substrate **1** by replacing the hydrogen atom of γ-CH_2 of **1a** with a methyl or dimethyl group. Thus, sterically demanding counterparts **1e** and **1f** afforded the corresponding products **3u**[10] and **3v** in 80% and 90% yields, respectively, but more severe reaction conditions (70 °C or 24 h) were required, illustrating that steric hindrance is evident in this domino reaction (Table 3, entries 11 and 12).

A proposed mechanism based on these experimental results and previous reports[11] are shown in Scheme 2. Initially, oxidative addition of the OH bond of AcOH to a palladium(0), formed *in situ* by reduction of $Pd(OAc)_2$, generated an initial H−Pd−OAc species.[11d] Subsequently, the syn addition of the H−Pd−OAc species to the triple bond of the alkynylphosphonate **1** led to an alkenylpalladium intermediate **B** with the observed regio- and stereochemistry. The reductive elimination of the intermediate **C** would produce the intermediate **D** and regenerate the Pd(0) species as a catalytically active species.

DOI: 10.1021/acs.joc.5b00999
J. Org. Chem. 2015, 80, 6908−6914

Table 2. Domino Addition−Cyclization of Diethyl (3-Hydroxyprop-1-yn-1-yl)phosphonate with Arylboronic Acids[a]



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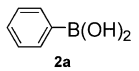
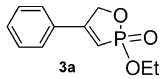
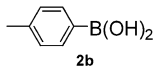
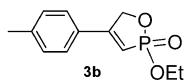
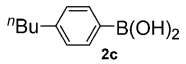
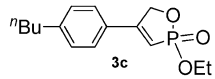
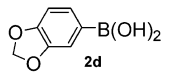
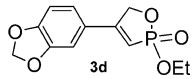
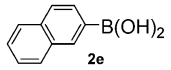
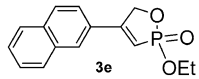
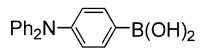
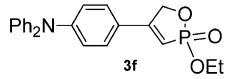
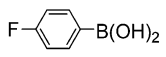
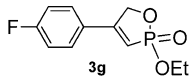
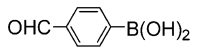
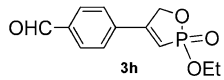
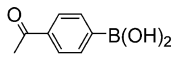
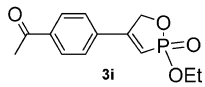
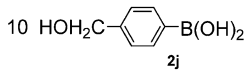
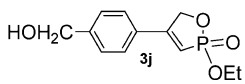
1	 2a	 3a	98
2	 2b	 3b	98
3	 2c	 3c	91
4	 2d	 3d	98
5	 2e	 3e	76
6	 2f	 3f	78
7	 2g	 3g	81[b]
8	 2h	 3h	46[b]
9	 2i	 3i	61[b]
10	 2j	 3j	52[b]

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.24 mmol), AcOH (10 mol %), $Pd(OAc)_2$ (3 mol %), dppb (6 mol %), 1,4-dioxane (1.0 mL), 60 °C, 12 h, under Ar. [b]70 °C.

Finally, **D** underwent an intramolecular nucleophilic substitution to give the desired product **3** and release one molecular alcohol.

In conclusion, we have developed a simple and efficient palladium-catalyzed domino addition−cyclization for the one-step synthesis of a series of valuable 1,2-oxaphosphole-3-ene 2-oxides starting from readily available arylboronic acids with 3-hydroxyprop-1-yn-1-yl phosphonates. Mechanistic studies revealed that the domino reaction involved a Michael addition followed by an intramolecular nucleophilic substitution. The described protocol has noticeable advantages, including operational simplicity, mild reaction conditions, remarkable functional group tolerance, and easy workup, and would provide a practical and powerful synthetic tool for the preparation of a variety of this new type of potential biological active organophosphorus heterocycles.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in tubes under argon. All the 3-hydroxyprop-1-yn-1-yl-phosphonates were prepared according to ref 11. All the other reagents were purchased from commercial sources and used without further purification. Column chromatography was performed on silica gel 300−400 mesh. ^1H, ^{13}C, and ^{31}P NMR spectra were measured on a 500 MHz spectrometer with $CDCl_3$ as solvent using tetramethylsilane (TMS) as the internal standard and 85% H_3PO_4 as the external standard for ^{31}P NMR. All compounds were further characterized by HRMS (FT-ICR-MS or TOF-MS).

General Procedure for the Synthesis of 3a−3v. An oven-dried tube with dppb (0.012 mmol), $Pd(OAc)_2$ (0.006 mmol), and arylboronic acid (0.24 mmol) was evacuated and purged with argon more than three times. A mixture of AcOH (0.020 mmol), 3-hydroxyprop-1-yn-1-yl-phosphonate (0.20 mmol), and 1,4-dioxide (1.0 mL) were added to the tube. The resulting mixture was stirred at the indicated temperature for 12 or 24 h. The product was purified directly by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent.

Spectral Data of the Compounds. *2-Ethoxy-4-phenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3a**, New Compound).* Solid, mp 172−174 °C, 43.5 mg, 98% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.37−7.36 (m, 5 H), 6.33−6.27 (dt apparent d, J = 30.7 Hz, 1 H), 5.09−5.00 (m, 2 H), 4.12−4.06 (dq apparent p, J = 7.7, 8.1 Hz, 2 H), 1.30 (t, J = 7.0 Hz, 3 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 158.2 (d, J_{C-P} = 20.9 Hz), 131.3 (d, J_{C-P} = 22.1 Hz), 131.0, 129.1, 125.8, 108.5 (d, J_{C-P} = 171.9 Hz), 70.1 (d, J_{C-P} = 9.7 Hz), 63.2 (d, J_{C-P} = 6.4 Hz), 16.4 (d, J_{C-P} = 6.2 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 44. IR (film) υ_{max}: 2921, 2851, 1604, 1573, 1497, 1449, 1219, 1194, 1132, 1077, 1039, 995, 970, 888, 801 cm^{-1}. HRMS m/z (ESI): calcd for $C_{11}H_{13}O_3P$ $[M + H]^+$: 225.0681, found: 225.0670.

*2-Ethoxy-4-(p-tolyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3b**, New Compound).* Solid, mp 213−215 °C, 46.7 mg, 98% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.34−7.32 (m, 2 H), 7.24−7.22 (m, 2 H), 6.35−6.27 (dt, J = 31.0, 1.7 Hz, 1 H), 5.12−5.07 (m, 2 H), 4.18−4.13 (m, 2 H), 2.39 (s, 3 H), 1.37 (t, J = 7.1 Hz, 3 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 158.1 (d, J_{C-P} = 20.8 Hz), 141.5, 129.7, 128.5 (d, J_{C-P} = 21.9 Hz), 125.7, 107.3 (d, J_{C-P} = 172.4 Hz), 70.1 (d, J_{C-P} = 9.4 Hz), 63.0 (d, J_{C-P} = 6.4 Hz), 21.3, 16.4 (d, J_{C-P} = 6.2 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 44. IR (film) υ_{max}: 2917, 2850, 1599, 1541, 1451, 1195, 1132, 1077, 1033, 973, 798 cm^{-1}. HRMS m/z (ESI): calcd for $C_{12}H_{15}O_3P$ $[M + H]^+$: 239.0837, found: 239.0829.

*4-(4-Butylphenyl)-2-ethoxy-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3c**, New Compound).* Solid, mp 168−169 °C, 50.8 mg, 91% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 7.36−7.35 (m, 2 H), 7.27−7.23 (m, 2 H), 6.35−6.28 (dt, J = 31.1, 2.5 Hz, 1 H), 5.16−5.05 (m, 2 H), 4.17−4.13 (m, 2 H), 2.64 (t, J = 15.5 Hz, 2 H), 1.63−1.57 (m, 2 H), 1.38−1.35 (m, 5 H), 0.93 (t, J = 7.4 Hz, 3 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 158.2 (d, J_{C-P} = 20.8 Hz), 146.5, 129.1, 128.7 (d, J_{C-P} = 22.1 Hz), 125.8, 107.3 (d, J_{C-P} = 172.4 Hz), 70.1 (d, J_{C-P} = 9.3 Hz), 63.1 (d, J_{C-P} = 6.4 Hz), 35.4, 33.2, 22.2, 16.4 (d, J_{C-P} = 6.2 Hz), 13.8. ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 44. IR (film) υ_{max}: 2956, 2927, 2873, 2858, 1600, 1562, 1514, 1218, 1192, 1132, 1071, 1040, 994, 967, 892, 799 cm^{-1}. HRMS m/z (ESI): calcd for $C_{15}H_{21}O_3P$ $[M + H]^+$: 281.1307, found: 281.1301.

*4-(Benzo[d][1,3]dioxol-5-yl)-2-ethoxy-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3d**, New Compound).* Solid, mp 229−231 °C, 53.0 mg, 98% yield. ^1H NMR (500 MHz, $CDCl_3$): δ 6.94−6.90 (m, 2 H), 6.85−6.83 (m, 1 H), 6.24−6.18 (dt apparent dd, J = 30.5, 0.9 Hz, 1 H), 6.03 (s, 2 H), 5.10−5.00 (m, 2 H), 4.19−4.13 (dq apparent p, J = 8.0, 7.3 Hz, 2 H), 1.37 (t, J = 7.1 Hz, 3 H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 157.5 (d, J_{C-P} = 21.5 Hz), 150.0, 148.5, 125.4 (d, J_{C-P} = 22.6 Hz), 120.3, 108.6, 106.7 (d, J_{C-P} = 172.9 Hz), 106.1, 101.7, 70.0 (d, J_{C-P} = 9.2 Hz), 63.1 (d, J_{C-P} = 6.4 Hz), 16.4 (d, J_{C-P} = 6.1 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 44. IR (film) υ_{max}: 2955, 2923, 2852, 1588, 1505, 1494, 1451, 1235, 1196, 1133, 1077, 1029, 968, 881, 832, 799 cm^{-1}. HRMS m/z (ESI): calcd for $C_{12}H_{13}O_5P$ $[M + H]^+$: 269.0579, found: 269.0571.

DOI: 10.1021/acs.joc.5b00999
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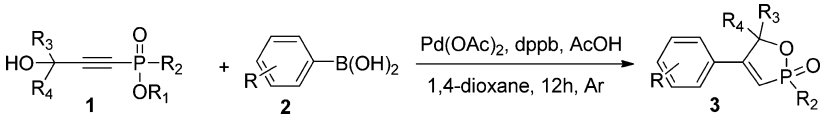
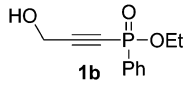
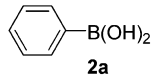
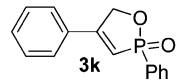
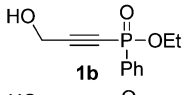
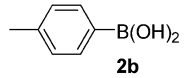
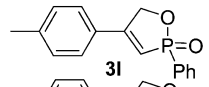
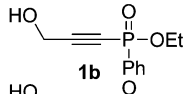
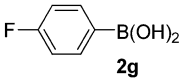
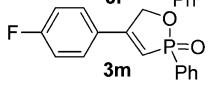
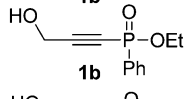
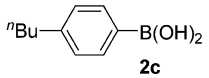
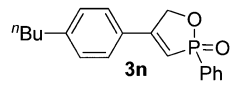
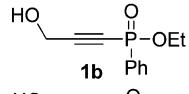
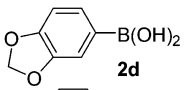
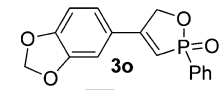
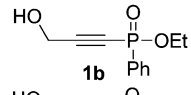
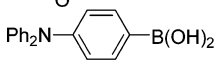
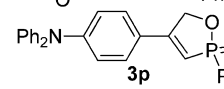
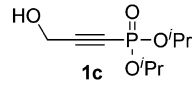
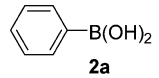
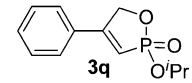
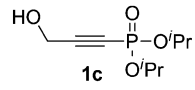
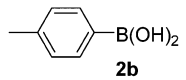
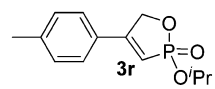
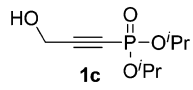
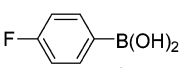
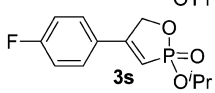
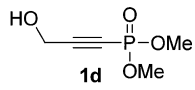
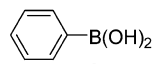
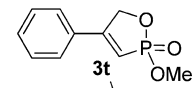
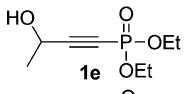
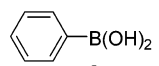
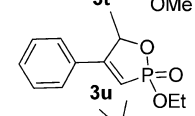
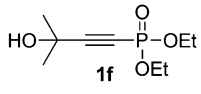
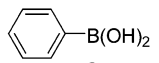
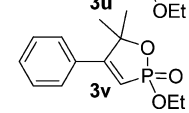
Table 3. Domino Addition−Cyclization of (3-Hydroxyprop-1-yn-1-yl)phosphonates with Arylboronic Acids[a]



entry	1	2	3	yield (%)
1				64
2				98
3				72[b]
4				98
5				96
6				94
7				47
8				72
9				58[b]
10				95
11				80[b]
12				90[c]

[a]Reaction conditions: **1** (0.20 mmol), **2** (0.24 mmol), AcOH (10 mol %), $Pd(OAc)_2$ (3 mol %), dppb (6 mol %), 1,4-dioxane (1.0 mL), 60 °C, 12 h, under Ar. [b]70 °C, 12 h. [c]70 °C, 24 h.

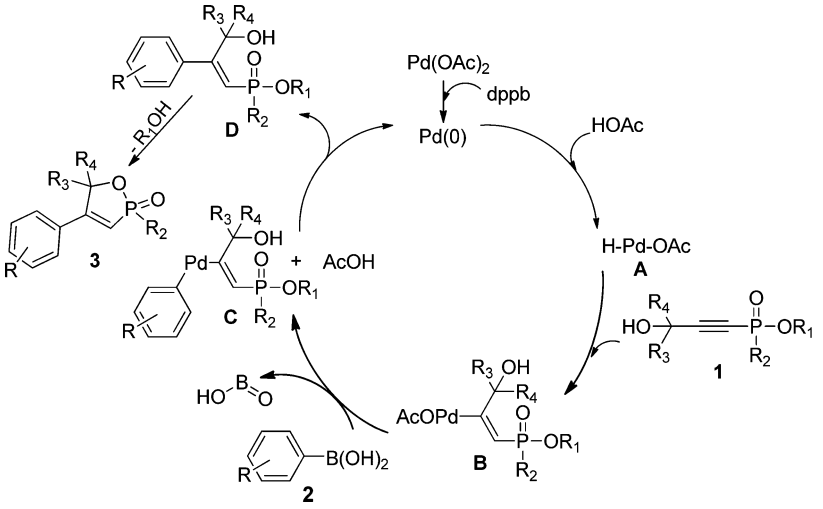
*2-Ethoxy-4-(naphthalen-2-yl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3e**, New Compound).* Solid, mp 207−209 °C, 41.4 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90−7.84 (m, 3 H), 7.85−7.79 (m, 1 H), 7.60−7.54 (m, 3 H), 6.52−6.46 (dt, J = 30.6, 1.9 Hz, 1 H), 5.30−5.20 (m, 2 H), 4.23−4.17 (m, 2 H), 1.39 (t, J = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.9 (d, J_{C-P} = 20.9 Hz), 134.2, 132.8, 129.0, 128.6, 128.58 (d, J_{C-P} = 22.0 Hz), 127.7 (d, J_{C-P} = 7.8 Hz), 127.1, 125.5, 123.0, 108.9 (d, J_{C-P} = 172.1 Hz), 70.1 (d, J_{C-P} = 9.2 Hz), 63.2 (d, J_{C-P} = 6.4 Hz), 16.5 (d, J_{C-P} = 5.8 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 44. IR (film) υ_{max}: 2922, 2851, 1659, 1632, 1589, 1468, 1196, 1132, 1077, 1040, 978, 894 804 cm^{-1}. HRMS m/z (ESI): calcd for $C_{15}H_{15}O_3P$ [M + H]$^+$: 275.0837, found: 275.0829.

*4-(4-(Diphenylamino)phenyl)-2-ethoxy-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3f**, New Compound).* Solid, mp 216−218 °C, 60.9 mg, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24−7.17 (m, 6 H), 7.05−7.03 (m, 6 H), 6.94−6.93 (m, 2 H), 6.14−6.07 (dt apparent d, J = 31.0 Hz, 1 H), 5.04−4.94 (m, 2 H), 4.07−4.04 (m, 2 H), 1.28 (t, J = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.6 (d, J_{C-P} = 20.9 Hz), 150.3, 146.6, 129.5, 126.8, 125.5, 124.3, 123.6 (d, J_{C-P}= 22.4 Hz), 121.2, 105.1 (d, J_{C-P} = 173.6 Hz), 70.0 (d, J_{C-P} = 9.8 Hz), 63.0 (d, J_{C-P} = 6.4 Hz), 16.4 (d, J_{C-P} = 6.1 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 45. IR (film) υ_{max}: 2923, 2851, 1590, 1509, 1488, 1282, 1195, 1132, 1077, 1041, 1000, 968, 887, 800 cm^{-1}. HRMS m/z (ESI): calcd for $C_{23}H_{22}NO_3P$ [M + H]$^+$: 392.1416, found: 392.1406.

*2-Ethoxy-4-(4-fluorophenyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3g**, New Compound).* Solid, mp 197−198 °C, 39.0 mg, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39−7.36 (m, 2 H), 7.07−7.04 (m, 2 H), 6.28−6.22 (dt apparent d, J = 30.4 Hz, 1 H), 5.03−5.00 (m, 2 H), 4.11−4.06 (m, 2 H), 1.29 (t, J = 6.9 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.1 (d, J_{C-F} = 252.9 Hz), 157.0 (d, J_{C-P} = 21.0 Hz), 127.9 (d, J_{C-F} = 8.3 Hz), 127.5 (dd, J_{C-F} = 22.4 Hz, J_{C-P} = 3.4 Hz), 116.3 (d, J_{C-F} = 22.4 Hz), 108.3 (d, J_{C-P} = 172.0 Hz), 69.9 (d, J_{C-P} = 9.2 Hz), 63.2 (d, J_{C-P} = 6.5 Hz), 16.4 (d, J_{C-P} = 5.6 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 44. IR (film) υ_{max}: 2923, 2853, 1607, 1510, 1453, 1236, 1194, 1163, 1132, 1077, 1036, 996, 969, 889, 799 cm^{-1}. HRMS m/z (ESI): calcd for $C_{11}H_{12}FO_3P$ [M + H]$^+$: 243.0586, found: 243.0579.

DOI: 10.1021/acs.joc.5b00999
J. Org. Chem. 2015, 80, 6908−6914

Scheme 2. Plausible Mechanism



*4-(2-Ethoxy-2-oxido-2,5-dihydro-1,2-oxaphosphol-4-yl)-benzaldehyde (**3h**, New Compound).* Wax solid, 23.2 mg, 46% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.00 (s, 1 H), 7.89−7.88 (m, 2 H), 7.54−7.52 (m, 2 H), 6.50−6.44 (dt, J = 29.9, 2.1 Hz, 1 H), 5.12−5.03 (m, 2 H), 4.18−4.12 (m, 2 H), 1.32 (t, J = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 191.1, 156.6 (d, J_{C-P} = 21.1 Hz), 137.7, 136.7 (d, J_{C-P} = 22.0 Hz), 130.3, 126.6, 112.2 (d, J_{C-P} = 170.9 Hz), 69.9 (d, J_{C-P} = 9.1 Hz), 63.6 (d, J_{C-P} = 6.5 Hz), 16.5 (d, J_{C-P} = 5.8 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 42. IR (film) υ_{max}: 2923, 2852, 1701, 1659, 1574, 1462, 1367, 1196, 1132, 1077, 1041, 973, 890, 801 cm^{-1}. HRMS m/z (ESI): calcd for $C_{12}H_{13}O_4P$ [M + Na]$^+$: 275.0449, found: 275.0453.

*1-(4-(2-Ethoxy-2-oxido-2,5-dihydro-1,2-oxaphosphol-4-yl)-phenyl)ethanone (**3i**, New Compound).* Solid, mp 231−232 °C, 32.5 mg, 61% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95−7.94 (m, 2 H), 7.47−7.46 (m, 2 H), 6.46−6.40 (dt, J = 30.2, 1.9 Hz, 1 H), 5.12−5.02 (m, 2 H), 4.17−4.11 (m, 2 H), 2.56 (s, 3 H), 1.32 (t, J = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 197.0, 156.8 (d, J_{C-P} = 21.3 Hz), 138.6, 135.4 (d, J_{C-P} = 22.0 Hz), 129.0, 126.2, 111.4 (d, J_{C-P} = 171.1 Hz), 69.9 (d, J_{C-P} = 9.1 Hz), 63.5 (d, J_{C-P} = 6.6 Hz), 26.7, 16.5 (d, J_{C-P} = 6.2 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 43. IR (film) υ_{max}: 2955, 2924, 2853, 1683, 1652, 1600, 1455, 1408, 1361, 1267, 1196, 1132, 1077, 1040, 973, 885, 802 cm^{-1}. HRMS m/z (ESI): calcd for $C_{13}H_{15}O_4P$ [M + H]$^+$: 267.0786, found: 267.0777.

*2-Ethoxy-4-(4-hydroxyphenyl)-2,5-dihydro-1,2-oxaphosphole 2-oxide (**3j**, New Compound).* Solid, mp 173−174 °C, 26.0 mg, 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43−7.42 (m, 2 H), 7.34−7.32 (m, 2 H), 6.25−6.18 (dt apparent d, J = 30.9 Hz, 1 H), 5.03−4.91 (m, 2 H), 4.73 (s, 2 H), 4.16−4.10 (m, 2 H), 1.35 (t, J = 7.1 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.0 (d, J_{C-P} = 20.9 Hz), 145.0, 129.9 (d, J_{C-P} = 22.2 Hz), 127.2, 125.9, 107.7 (d, J_{C-P} = 172.4 Hz), 70.1 (d, J_{C-P} = 9.6 Hz), 64.1, 63.3 (d, J_{C-P} = 6.5 Hz), 16.4 (d, J_{C-P} = 6.0 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 44. IR (film) υ_{max}: 3195, 2955, 2922, 2851, 1659, 1632, 1468, 1411, 1377, 1196, 1132, 1077, 1039, 973, 889, 800 cm^{-1}. HRMS m/z (ESI): calcd for $C_{12}H_{15}O_4P$ [M + H]$^+$: 255.0786, found: 255.0777.

*2,4-Diphenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3k**, New Compound).* Solid, mp 139−140 °C, 32.8 mg, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73−7.70 (m, 2 H), 7.51−7.48 (m, 1 H), 7.43−7.37 (m, 7 H), 6.50−6.43 (dt, J = 32.8, 2.0 Hz, 1 H), 5.43−5.39 (m, 1 H), 5.30−5.24 (m, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.8 (d, J_{C-P} = 16.1 Hz), 132.7 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 11.4 Hz), 131.2 (d, J_{C-P} = 18.2 Hz), 131.0, 130.9 (d, J_{C-P} = 141.7 Hz), 129.1, 128.6 (d, J_{C-P} = 14.1 Hz), 126.2, 113.5 (d, J_{C-P} = 120.6 Hz), 73.7 (d, J_{C-P} = 3.1 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 58. IR (film) υ_{max}: 2922, 2852, 2355, 1652, 1601, 1573, 1495, 1440, 1346, 1223, 1195, 1132, 1077, 1035, 973, 877, 817 cm^{-1}. HRMS m/z (ESI): calcd for $C_{15}H_{13}O_2P$ [M + Na]$^+$: 279.0551, found: 279.0554.

*2-Phenyl-4-(p-tolyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3l**, New Compound).* Solid, mp 165−167 °C, 53.0 mg, 98% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81−7.76 (m, 2 H), 7.56−7.55 (m, 1 H), 7.49−7.46 (m, 2 H), 7.39−7.38 (m, 2 H), 7.27−7.24 (m, 2 H), 6.51−6.45 (dt apparent d, J = 32.9 Hz, 1 H), 5.48−5.45 (m, 1 H), 5.35−5.32 (m, 1 H), 2.40 (s, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.8 (d, J_{C-P} = 16.1 Hz), 141.5, 132.6 (d, J_{C-P} = 3.0 Hz), 131.8 (d, J_{C-P} = 11.5 Hz), 131.2 (d, J_{C-P} = 141.6 Hz), 129.8, 128.5 (d, J_{C-P} = 13.9 Hz), 128.4 (d, J_{C-P} = 18.2 Hz), 126.1, 112.3 (d, J_{C-P} = 121.3 Hz), 73.7 (d, J_{C-P} = 3.4 Hz), 21.4. ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 58. IR (film) υ_{max}: 2955, 2925, 2854, 1612, 1595, 1515, 1439, 1231, 1181, 1123, 1035, 1000, 971, 877, 800 cm^{-1}. HRMS m/z (ESI): calcd for $C_{16}H_{15}O_2P$ [M + H]$^+$: 271.0888, found: 271.0879.

*4-(4-Fluorophenyl)-2-phenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3m**, New Compound).* Solid, mp 142−145 °C, 39.5 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81−7.76 (m, 2 H), 7.60−7.56 (m, 1 H), 7.51−7.47 (m, 4 H), 7.16−7.13 (m, 2 H), 6.53−6.46 (dt, J = 32.3, 1.9 Hz, 1 H), 5.47−5.43 (m, 1 H), 5.35−5.29 (m, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.1 (d, J_{C-F} = 252.5 Hz), 156.5 (d, J_{C-P} = 16.3 Hz), 132.8 (d, J_{C-F} = 3.0 Hz), 131.8 (d, J_{C-P} = 11.6 Hz), 130.9 (d, J_{C-P} = 141.8 Hz), 128.6 (d, J_{C-P} = 13.8 Hz), 128.2 (d, J_{C-P} = 8.6 Hz), 127.5 (dd, J_{C-P} = 18.7, 3.4 Hz), 116.3 (d, J_{C-P} = 21.9 Hz), 113.5 (dd, J_{C-P} = 120.7 Hz, J_{C-F} = 1.5 Hz), 73.6 (d, J_{C-P} = 2.9 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 58. IR (film) υ_{max}: 3057, 2955, 2925, 2864, 1594, 1572, 1496, 1448, 1439, 1238, 1194, 1123, 1035, 1000, 972, 873, 800 cm^{-1}. HRMS m/z (ESI): calcd for $C_{15}H_{12}FO_2P$ [M + H]$^+$: 275.0637, found: 275.0629.

*4-(4-Butylphenyl)-2-phenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3n**, New Compound).* Wax solid, 61.2 mg, 98% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80−7.76 (m, 2 H), 7.57−7.54 (m, 1 H), 7.49−7.47 (m, 2 H), 7.41−7.40 (m, 2 H), 7.27−7.25 (m, 2 H), 6.52−6.45 (dt apparent d, J = 32.9 Hz, 1 H), 5.48−5.45 (m, 1 H), 5.35−5.30 (m, 1 H), 2.65 (t, J = 7.7 Hz, 2 H), 1.64−1.58 (m, 2 H), 1.40−1.32 (m, 2 H), 0.94 (t, J = 7.3 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.8 (d, J_{C-P} = 16.1 Hz), 146.5, 132.6 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 11.5 Hz), 131.2 (d, J_{C-P} = 141.5 Hz), 129.2, 128.6 (d, J_{C-P} = 18.0 Hz, overlapped), 128.5 (d, J_{C-P} = 13.9 Hz, overlapped), 126.2, 112.3 (d, J_{C-P} = 121.3 Hz), 73.7 (d, J_{C-P} = 3.5 Hz), 35.5, 33.3, 22.3, 13.9. ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 58. IR (film) υ_{max}: 2922, 2852, 1651, 1594, 1557, 1439, 1384, 1196, 1132, 1077, 1034, 973, 804 cm^{-1}. HRMS m/z (ESI): calcd for $C_{19}H_{21}O_2P$ [M + H]$^+$: 313.1357, found: 313.1349.

*4-(Benzo[d][1,3]dioxol-5-yl)-2-phenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**30**, New Compound).* Solid, mp 115−116 °C, 57.4 mg, 96% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72−7.68 (m, 2 H), 7.50−7.47 (m, 1 H), 7.42−7.38 (m, 2 H), 6.91−6.88 (m, 2 H), 6.79−6.77 (m, 1 H), 6.33−6.26 (dt, J = 32.2, 1.9 Hz, 1 H), 5.96 (s, 2H), 5.36−5.32 (m, 1 H), 5.23−5.17 (m, 1 H). ^{13}C{^{1}H} NMR (125 MHz,

DOI: 10.1021/acs.joc.5b00999
J. Org. Chem. 2015, 80, 6908−6914

$CDCl_3$): δ 157.2 (d, J_{C-P} = 16.4 Hz), 149.9, 148.5, 132.6 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 11.2 Hz), 131.1 (d, J_{C-P} = 141.8 Hz), 128.6 (d, J_{C-P} = 14.1 Hz), 125.3 (d, J_{C-P} = 18.8 Hz), 120.7, 111.6 (d, J_{C-P} = 121.8 Hz), 108.6, 106.3, 101.7, 73.6 (d, J_{C-P} = 3.3 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 58. IR (film) υ_{max}: 2954, 2921, 2852, 1582, 1506, 1491, 1452, 1230, 1196, 1132, 1077, 1034, 932, 868, 802 cm^{-1}. HRMS *m*/*z* (ESI): calcd for $C_{16}H_{13}O_4P$ $[M + H]^+$: 301.0630, found: 301.0625.

*4-(4-(Diphenylamino)phenyl)-2-phenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3p**, New Compound).* Solid, mp 171−173 °C, 79.6 mg, 94% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71−7.67 (m, 2 H), 7.47−7.44 (m, 1 H), 7.39−7.36 (m, 2 H), 7.23−7.17 (m, 6 H), 7.05−7.01 (m, 6 H), 6.95−6.94 (m, 2 H), 6.30−6.23 (dt, *J* = 32.9, 1.7 Hz, 1 H), 5.36−5.32 (m, 1 H), 5.23−5.17 (m, 1 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.2 (d, J_{C-P} = 16.2 Hz), 150.3, 146.6, 132.5 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 11.3 Hz), 131.4 (d, J_{C-P} = 141.0 Hz), 129.5, 128.5 (d, J_{C-P} = 13.7 Hz), 127.2, 125.4, 124.2, 123.5 (d, J_{C-P} = 18.8 Hz), 121.3, 110.1 (d, J_{C-P} = 122.7 Hz), 73.6 (d, J_{C-P} = 3.5 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 59. IR (film) υ_{max}: 2955, 2921, 2851, 1588, 1511, 1489, 1237, 1196, 1132, 1077, 1034, 973, 876, 802 cm^{-1}. HRMS *m*/*z* (ESI): calcd for $C_{27}H_{22}NO_2P$ $[M + H]^+$: 424.1466, found: 424.1465.

*2-Isopropoxy-4-phenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3q**, New Compound).* Solid, mp 113−115 °C, 22.4 mg, 47% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.36 (m, 5 H), 6.32−6.26 (dt, *J* = 30.9, 2.0 Hz, 1 H), 5.08−4.99 (m, 2 H), 4.73−4.66 (m, 1 H), 1.31−1.29 (q, 6 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.7 (d, J_{C-P} = 20.9 Hz), 131.4 (d, J_{C-P} = 21.9 Hz), 130.9, 129.1, 125.8, 109.3 (d, J_{C-P} = 172.4 Hz), 72.0 (d, J_{C-P} = 6.4 Hz), 69.9 (d, J_{C-P} = 9.8 Hz), 24.0 (d, J_{C-P} = 3.8 Hz), 23.8 (d, J_{C-P} = 5.3 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 43. IR (film) υ_{max}: 2954, 2924, 2853, 1604, 1575, 1498, 1449, 1376, 1255, 1196, 1132, 1105, 1077, 1040, 1006, 997, 971, 884, 811 cm^{-1}. HRMS *m*/*z* (ESI): calcd for $C_{12}H_{15}O_3P$ $[M + H]^+$: 239.0837, found: 239.0830.

*2-Isopropoxy-4-(p-tolyl)-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3r**, New Compound).* Solid, mp 131−132 °C, 36.3 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34−7.32 (m, 2 H), 7.24−7.22 (m, 2 H), 6.33−6.27 (dt, *J* = 31.0, 1.6 Hz, 1 H), 5.13−5.04 (m, 2 H), 4.79−4.72 (m, 1 H), 2.39 (s, 3 H), 1.38−1.36 (q, 6 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 157.7 (d, J_{C-P} = 20.8 Hz), 141.3, 129.7, 128.6 (d, J_{C-P} = 21.9 Hz), 125.7, 108.0 (d, J_{C-P} = 173.1 Hz), 71.8 (d, J_{C-P} = 6.7 Hz), 69.9 (d, J_{C-P} = 9.5 Hz), 24.0 (d, J_{C-P} = 3.7 Hz), 23.8 (d, J_{C-P} = 5.3 Hz), 21.4. ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 43. IR (film) υ_{max}: 2955, 2925, 2854, 1612, 1595, 1515, 1439, 1373, 1231, 1195, 1132, 1105, 1077, 1035, 1001, 971, 897, 885, 808 cm^{-1}. HRMS *m*/*z* (ESI): calcd for $C_{13}H_{17}O_3P$ $[M + H]^+$: 253.0994, found: 253.0985.

*4-(4-Fluorophenyl)-2-isopropoxy-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3s**, New Compound).* Solid, mp 176−179 °C, 29.7 mg, 58% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38−7.35 (m, 2 H), 7.07−7.04 (m, 2 H), 6.27−6.21 (dt apparent d, *J* = 30.4 Hz, 1 H), 5.04−4.96 (m, 2 H), 4.75−4.69 (m, 1 H), 1.32−1.29 (q, 6 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.1 (d, J_{C-F} = 252.5 Hz), 156.5 (d, J_{C-P} = 21.4 Hz), 127.9 (d, J_{C-F} = 8.8 Hz), 127.7 (dd, J_{C-F} = 22.6, J_{C-P} = 3.6 Hz), 116.3 (d, J_{C-P} = 21.9 Hz), 109.3 (d, J_{C-P} = 174.0 Hz), 72.1 (d, J_{C-P} = 6.4 Hz), 69.8 (d, J_{C-P} = 9.2 Hz), 24.1 (d, J_{C-P} = 4.2 Hz), 23.8 (d, J_{C-P} = 5.4 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 43. IR (film) υ_{max}: 2953, 2924, 2853, 1606, 1511, 1461, 1377, 1239, 1195, 1132, 1077, 1042, 998, 972, 886, 803 cm^{-1}. HRMS *m*/*z* (ESI): calcd for $C_{12}H_{14}FO_3P$ $[M + H]^+$: 257.0743, found: 257.0723.

*2-Methoxy-4-phenyl-2,5-dihydro-1,2-oxaphosphole 2-oxide (**3t**, New Compound).* Solid, mp 167−170 °C, 40.0 mg, 95% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39−7.37 (m, 5 H), 6.33−6.27 (dt, *J* = 31.0, 1.8 Hz, 1 H), 5.12−5.01 (m, 2 H), 3.73 (d, *J* = 11.7 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 158.6 (d, J_{C-P} = 20.8 Hz), 131.3 (d, J_{C-P} = 21.8 Hz), 131.1, 129.2, 125.9, 108.1 (d, J_{C-P} = 171.8 Hz), 70.2 (d, J_{C-P} = 9.8 Hz), 53.5 (d, J_{C-P} = 6.7 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 45. IR (film) υ_{max}: 2923, 2852, 1659, 1602, 1494, 1441, 1367, 1350, 1306, 1195, 1132, 1077, 1041, 1025, 852 cm^{-1}. HRMS *m*/*z* (ESI): calcd for $C_{10}H_{11}O_3P$ $[M + H]^+$: 211.0524, found: 211.0518.

*2-Ethoxy-5-methyl-4-phenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3u**, New Compound; Many ^{1}H and ^{13}C NMR Signals Were Split Due to the Presence of (Phosphate) Diastereoisomers in the Sample).* Solid, mp 124−125 °C, 38.1 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37−7.31 (m, 5 H), 6.18−6.12 (dt apparent d, *J* = 30.3 Hz, 1 H), 5.47−5.38 (m, 1 H), 4.18−4.12 (m, 1.1 H), 4.09−4.03 (m, 0.9 H), 1.45−1.43 (d, *J* = 6.7 Hz, 1.4 H), 1.40−1.39 (d, *J* = 6.7 Hz, 1.6 H), 1.34−1.31 (t, *J* = 7.1 Hz, 1.6 H), 1.29−1.27 (t, *J* = 7.1 Hz, 1.4 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.00 (d, J_{C-P} = 19.9 Hz), 163.95 (d, J_{C-P} = 19.9 Hz), 132.4 (d, J_{C-P} = 22.2 Hz), 132.3 (d, J_{C-P} = 22.5 Hz), 130.4, 129.0, 126.7 (d, J_{C-P} = 3.3 Hz), 110.2 (d, J_{C-P} = 168.8 Hz), 110.0 (d, J_{C-P} = 170.6 Hz), 78.4 (d, J_{C-P} = 8.2 Hz), 78.0 (d, J_{C-P} = 8.2 Hz), 63.3 (d, J_{C-P} = 6.4 Hz), 63.0 (d, J_{C-P} = 6.4 Hz), 21.5 (d, J_{C-P} = 1.8 Hz), 21.0, 16.6 (d, J_{C-P} = 5.9 Hz), 16.4 (d, J_{C-P} = 5.9 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 39.8, 39.3. IR (film) υ_{max}: 2922, 2852, 1592, 1566, 1492, 1443, 1195, 1133, 1077, 1043, 972, 899, 856 cm^{-1}. HRMS *m*/*z* (ESI): calcd for $C_{12}H_{15}O_3P$ $[M + H]^+$: 239.0837, found: 239.0828.

*2-Ethoxy-5,5-dimethyl-4-phenyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (**3v**, New Compound).* Solid, mp 140−141 °C, 45.4 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34−7.32 (m, 3 H), 7.28−7.26 (m, 2 H), 5.96−5.90 (dt apparent d, *J* = 30.1 Hz, 1 H), 4.15−4.09 (m, 2 H), 1.55 (d, *J* = 5.9 Hz, 6 H), 1.31 (t, *J* = 7.0 Hz, 3 H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 169.0 (d, J_{C-P} = 17.5 Hz), 134.1 (d, J_{C-P} = 22.6 Hz), 129.4, 128.6, 127.3, 113.1 (d, J_{C-P} = 165.3 Hz), 87.4 (d, J_{C-P} = 7.6 Hz), 62.9 (d, J_{C-P} = 6.4 Hz), 27.8 (d, J_{C-P} = 3.1 Hz), 27.3 (d, J_{C-P} = 2.4 Hz), 16.6 (d, J_{C-P} = 5.6 Hz). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 35. IR (film) υ_{max}: 2951, 2923, 2851, 1595, 1572, 1497, 1448, 1220, 1195, 1132, 1077, 1043, 1006, 996, 911, 866, 821 cm^{-1}. HRMS *m*/*z* (ESI): calcd for $C_{13}H_{17}O_3P$ $[M + H]^+$: 253.0994, found: 253.0984.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectrum. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00999.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Chinese National Natural Science Foundation (21202135), the Natural Science Foundation of Fujian Province of China (No. 2013J05031) and the National Basic Research Program of China (2012CB821600).

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