JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Metal-Free Aromatic Carbon−Phosphorus Bond Formation via a Sandmeyer-Type Reaction

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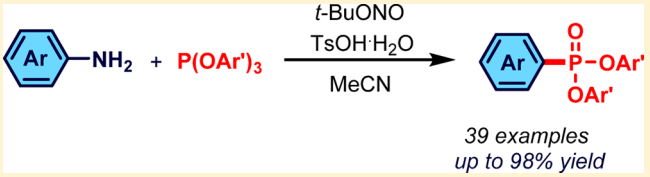
Supporting Information

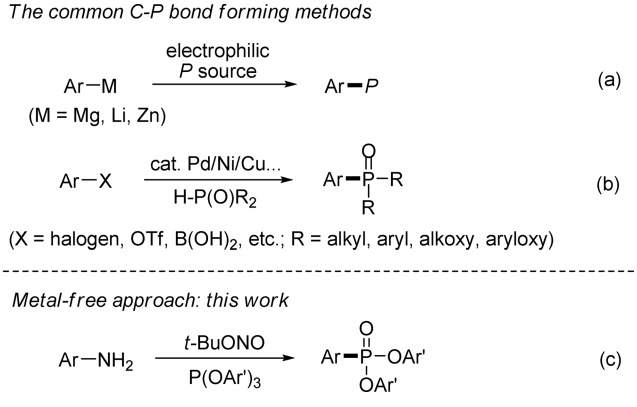
ABSTRACT: An efficient metal-free phosphorylation process based on a Sandmeyer-type transformation with arylamines as the starting materials is developed. The transformation proceeds smoothly at room temperature without the exclusion of moisture or air. This phosphorylation reaction tolerates a wide range of functional groups and affords the phosphorylation products in moderate to good yields, thus providing a valuable method for the formation of aromatic carbon−phosphorus bonds.



INTRODUCTION

Aryl phosphonates belong to an important class of organophosphorus compounds due to their applications in medicinal chemistry,[1] material sciences,[2] and organic synthesis,[3] which makes the synthesis of this type of compound of significant importance. Traditional methods to construct the aromatic carbon−phosphorus bonds in these compounds involve nucleophilic substitution reaction of organometallic reagent with electrophilic phosphine reagent (Scheme 1a),[4] Michaelis-Arbuzov reaction,[5] and Friedel−Crafts reaction.[6] Additionally, the transition-metal-catalyzed cross-coupling reaction of aryl (pseudo)halides or some other compounds, such as aryltriflates, tosylates, boronic acids, and hydrazine with phosphorus(III) compounds has been explored extensively since Hirao and co-workers' pioneering work in the 1980s.[7,8] Because of the excellent efficiency and remarkable functional group tolerance, the transition-metal-catalyzed coupling strategy has been widely utilized in carbon−phosphorus bond formation (Scheme 1b). Despite significant progress, these methods still suffer from some limitations, such as the use of metal reagents and the requirement of relatively high temperature. Further efforts were made to construct aromatic carbon−phosphorus bonds under mild conditions; for example, Xiao and co-workers have recently reported that the employment of visible-light-induced photoredox catalysis achieves the nickel-catalyzed cross-coupling of aryl halide with diarylphosphine oxides at room temperature;[9] Toste and co-workers reported that, by employing dual gold and photoredox catalysis, aryldiazonium salts could react with *H*-phosphonates at room temperature to form carbon−phosphorus bonds.[10] Despite these remarkable improvements, highly efficient approaches for the construction of an aromatic carbon−phosphorus bond under metal-free mild conditions, which could serve as alternative and supplementary methods for the synthesis of aryl phosphonate compounds, are still limited.

Scheme 1. Synthetic Methods for the Construction of Aromatic Carbon−Phosphorus Bonds



On the other hand, the transformation of aryldiazonium salts into various functional groups, such as halogen, hydroxyl group, cyano group, and sulfonates groups, known as Sandmeyer-type reactions, has been applied broadly both in laboratory research and industrial production.[11] The aryldiazonium salt intermediates, which could be in situ generated from aromatic amines,[12] has been recently explored in several new transformations.[13,14] We have recently reported new approaches for the synthesis of arylboronic pinacol esters, arylstannane compounds, and trifluoromethylated arenes by using readily available arylamines as the starting materials.[14] Aryldiazonium salts have been previously reported to react with phosphorus trihalides since the 1950s,[15] but these transformations often suffer from poor yields and limited functional group tolerance. In light of the importance of aryl phosphonates compounds and our continued interest in the development of transformations

Received: July 28, 2016
Published: October 28, 2016

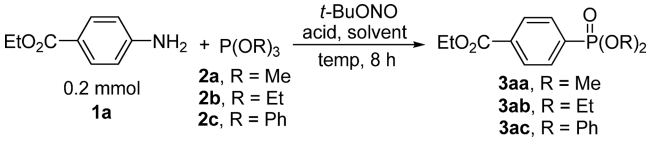
DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603−11611

with aryldiazonium salts, we report herein an efficient approach for the metal-free C−P bond formation through a similar Sandmeyer-type transformation. The important feature of this method is the use of triarylphosphites, which are stable and easy to handle, rather than the air-sensitive phosphorus trihalides, as the phosphorylation reagents.

RESULTS AND DISCUSSION

We began the study of the phosphorylation reaction with ethyl 4-aminobenzoate (**1a**) as the starting material. Arylamine **1a** was first reacted with *tert*-butyl nitrite (*t*-BuONO) in MeCN to form the corresponding aryldiazonium salt at 0 °C, and then trimethyl phosphite (**2a**) was added in sequence. To our delight, the expected phosphorylation product **3aa** was obtained at a yield of 44% (Table 1, entry 1). As detected by

Table 1. Optimization of Reaction Conditions[a]



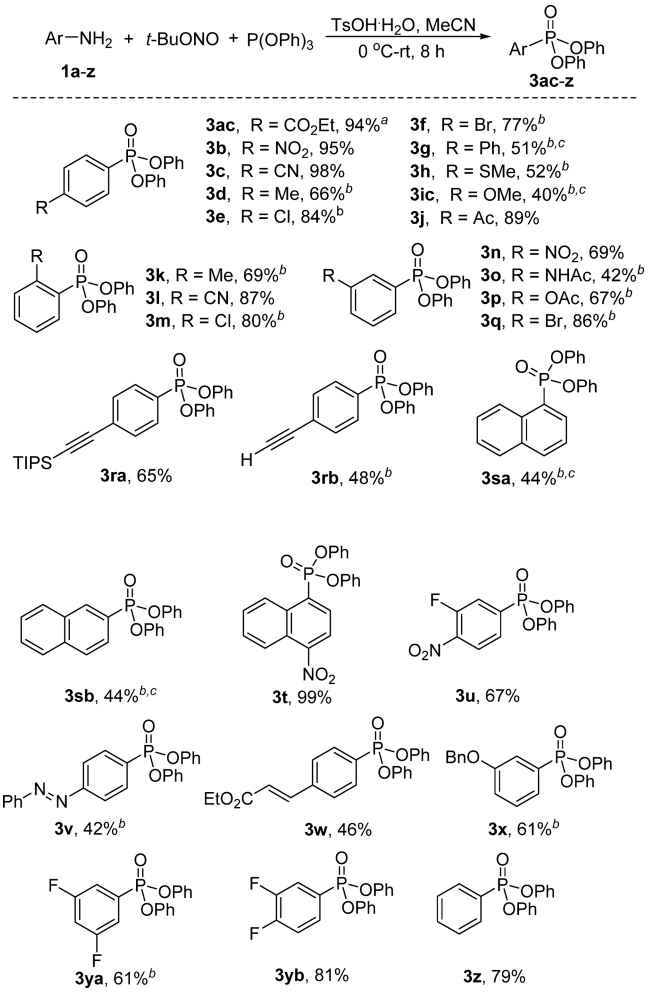
entry	acid	solvent	temp	2, R	3, yield (%)[b]
1	none	MeCN	0 °C−rt	**2a**, Me	**3aa**, 44
2	TsOH·H_2O	MeCN	0 °C−rt	**2a**, Me	**3aa**, 54
3	HCl	MeCN	0 °C−rt	**2a**, Me	**3aa**, 16
4	H_2SO_4	MeCN	0 °C−rt	**2a**, Me	**3aa**, 20
5	BF_3·Et_2O	MeCN	0 °C−rt	**2a**, Me	**3aa**, −
6	TsOH·H_2O	DCM	0 °C−rt	**2a**, Me	**3aa**, 44
7	TsOH·H_2O	DCE	0 °C−rt	**2a**, Me	**3aa**, 17
8	TsOH·H_2O	MeCN	0−80 °C	**2a**, Me	**3aa**, 54
9	TsOH·H_2O	MeCN	0 °C−rt	**2b**, Et	**3ab**, trace
10	TsOH·H_2O	MeCN	0 °C−rt	**2c**, Ph	**3ac**, 78
11[c]	TsOH·H_2O	MeCN	0 °C−rt	**2c**, Ph	**3ac**, 79
12[d]	TsOH·H_2O	MeCN	0 °C−rt	**2c**, Ph	**3ac**, 62
13[e]	TsOH·H_2O	MeCN	0 °C−rt	**2c**, Ph	**3ac**, 51
14[f]	TsOH·H_2O	MeCN	0 °C−rt	**2c**, Ph	**3ac**, 94

[a]Unless otherwise noted, the reaction conditions are as follows: arylamine (0.2 mmol), *t*-BuONO (0.3 mmol), $P(OR)_3$ (0.4 mmol), acid (0.24 mmol), solvent (1.0 mL). Arylamine first reacted with *t*-BuONO and acid at 0 °C for 15 min, and then the reaction system was allowed to warm to room temperature and $P(OR)_3$ was added. [b]Isolated yield. [c]Using 0.5 mL of solvent. [d]Added 0.3 mmol $P(OR)_3$. [e]Added 0.24 mmol *t*-BuONO. [f]Added 0.6 mmol $P(OR)_3$.

GC-MS, the major byproducts were ethyl benzoate, which was generated by the reduction of aryldiazonium salt species, and trimethyl phosphate. Because our previous study indicated that acid can promote the generation of diazonium intermediate,[14c] we thus proceeded to study the effect of acid additives. Indeed, the reaction proceeded more efficiently when TsOH was added (Table 1, entry 2); however, HCl and H_2SO_4 were found to not be suitable for this transformation (Table 1, entries 3 and 4), and the reaction failed to give **3aa** when typical Lewis acid BF_3·Et_2O was added (Table 1, entry 5). Product **3aa** was formed at a lower yield when the reaction was carried out in dichloromethane (DCM) or dichloroethane (DCE) (Table 1, entries 6 and 7). No apparent improvement was observed when the reaction temperature was raised to 80 °C (Table 1, entry 8). Some other phosphorylation reagents were then explored. Triethyl phosphite (**2b**) gave only a trace amount of corresponding product **3ab** (detected by GC-MS; Table 1, entry 9). Moreover, only a trace amount of ethyl benzoate was observed because aryldiazonium salt was mainly transformed into some nonvolatile species under this condition. To our delight, when triphenyl phosphite (**2c**) was employed as the phosphorus source, corresponding product **3ac** was produced with a yield of 78% (Table 1, entry 10). The increase of concentration showed almost no influence on the transformation (Table 1, entry 11). A low loading of *t*-BuONO and **2c** led to diminished yields of **3ac** (Table 1, entries 12 and 13). The yield of **3ac** could be further improved with a higher loading of **2c** (Table 1, entry 14). One likely explanation for this result is that the higher equivalent of **3c** accelerates the phosphorylation process so that the generation of ethyl benzoate is inhibited.

With the optimized reaction conditions in hand, we then examined the substrate scope of this transformation with a series of functionalized arylamines using **2c** as the phosphorylation reagent (Scheme 2). The phosphorylation process has shown good functional group tolerance to both electron-

Scheme 2. Substrate Scope of the Aniline Derivatives[d]



[a]Isolated yield after column chromatography. [b]The reaction of arylamine with *t*-BuONO was carried out at room temperature for 10 min. [c]Added 3.0 mL of MeCN. [d]Reaction conditions: arylamine (0.2 mmol), *t*-BuONO (0.3 mmol), $P(OPh)_3$ (0.6 mmol), TsOH·H_2O (0.24 mmol), MeCN (1.0 mL). Arylamine was first reacted with *t*-BuONO and acid at 0 °C for 15 min, and then the reaction system was warmed to room temperature and $P(OPh)_3$ was added.

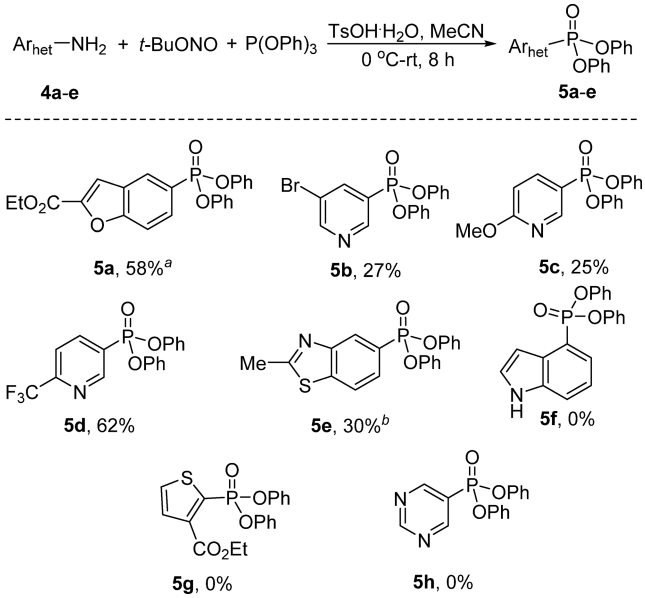
DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603−11611

withdrawing and -donating groups on the aromatic ring, including nitro (**3b**), cyano (**3c**), methyl (**3d**), halogen (**3e** and **3f**), phenyl (**3g**), methylthio (**3h**), methoxy (**3ic**), acetyl (**3j**), alkynyl (**3ra** and **3rb**), alkenyl (**3w**), azo group (**3v**), and hydrogen (**3z**). In all cases, the corresponding products were obtained in 40−98% yields. It is noteworthy that the tolerances of bromo and chloro groups, which are normally not compatible in transition-metal-catalyzed C−P bond construction approaches, make possible further transformation of the products with cross-coupling reactions.

The *para*-substituted aryl amines with electron-withdrawing groups could gave relatively higher yields, whereas the substrate with electron-donating *para*-methyl substituent afforded a moderate yield of 66% (**3d**). The *p*-OMe-substituted aniline gave a low yield of 40% (**3ic**). A similar yield could be achieved with *ortho*- and *meta*-substituted anilines (**3k−q**), indicating that the phosphorylation is not sensitive to the steric effect. For the naphthylamine **1sa** and **1sb**, the diminished yield might be attributed to the poor solubility of the corresponding diazonium salts.

We then expended the substrate scope of this phosphorylation reaction to the aromatic heterocyclic amine derivatives. The results shown in Scheme 3 indicate that the phosphorylation of some aromatic heterocyclic amine derivatives also work but give the phosphorylation products in low yields (**5a−e**). However, the phosphorylation reaction with some other aromatic heterocyclic amine derivatives did not occur (**5f−h**).

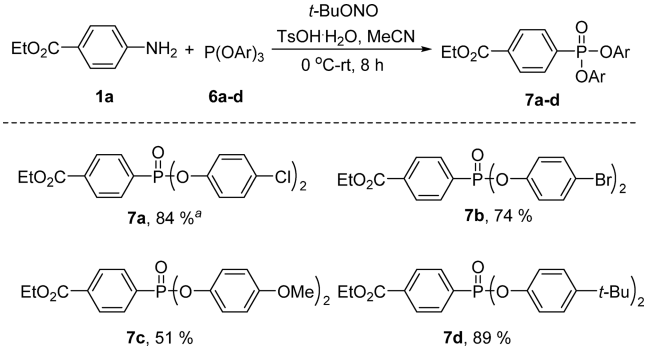
Scheme 3. Substrate Scope of Aromatic Heterocyclic Amine Derivatives[c]



[a]Isolated yield with column chromatography. [b]The reaction of arylamine with *t*-BuONO was carried out at room temperature for 10 min. [c]Unless otherwise noted, the reaction conditions are as follows: arylamine (0.2 mmol), *t*-BuONO (0.3 mmol), P(OPh)$_3$ (0.6 mmol), TsOH·H$_2$O (0.24 mmol), MeCN (1.0 mL). Arylamine first reacted with *t*-BuONO and acid at 0 °C for 15 min, and then the reaction system was warmed to room temperature and P(OPh)$_3$ was added.

Next, the scope of a series of substituted triaryl phosphites (**6a−d**) was investigated, and the results are summarized in Scheme 4. Good yields were achieved for the chloro (**7a**)- and bromo (**7b**)-substituted products, which could be convenient for further modifications. The *tert*-butyl-substituted phosphite also gave a good yield of 89% (**7d**), but the reaction with methoxy-substituted substrate gave only diminished yield (**7c**).

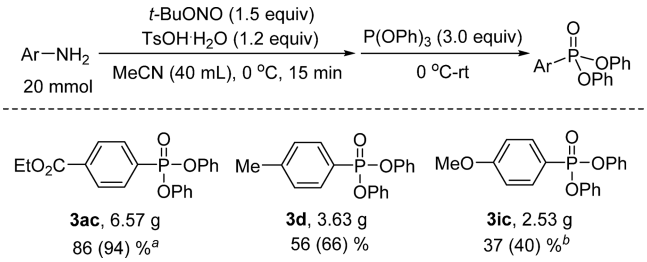
Scheme 4. Substrate Scope of the Triaryl Phosphites[b]



[a]Isolated yield after column chromatography. [b]Reaction conditions: arylamine (0.2 mmol), *t*-BuONO (0.3 mmol), P(OAr)$_3$ (0.6 mmol), TsOH·H$_2$O (0.24 mmol), MeCN (1.0 mL). Arylamine first reacted with *t*-BuONO and acid at 0 °C for 15 min, and then the reaction system was warmed to room temperature and P(OPh)$_3$ was added.

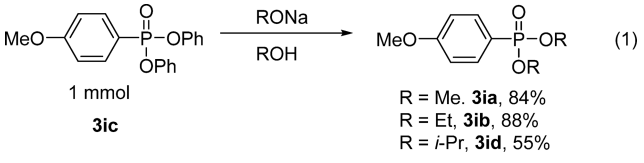
For a further demonstration of the practical application of this method, the phosphorylation reaction of three substrates was carried out in 20 mmol scale for the gram-scale synthesis of products **3ac**, **3d**, and **3ic**, as shown in Scheme 5. To our delight, the reaction offered the corresponding products with comparable yields.

Scheme 5. Gram-Scale Synthesis



[a]Isolated yield, the numbers in the brackets are the yields for the reaction carried out in 0.2 mmol-scale. [b]The reaction of arylamine with *t*-BuONO was carried out at room temperature for 10 min.

It is worth mentioning that the reaction using trialkyl phosphite (Table 1, **2a**, **2b**) as the phosphorylation reagent could only give a low yield, which might be a potential limit for the practical usefulness of this phosphorylation reaction. However, it was shown that the diphenyl phosphonates could be easily transferred to various dialkyl phosphonates through ester exchange as demonstrated by the example shown in eq 1,[16] which could circumvent such a limitation.

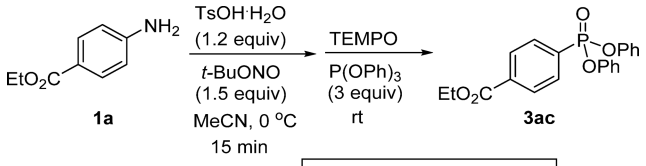


The mechanism of the reaction between arenediazonium salts and some phosphorus(III) compounds was previously

DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603−11611

investigated by Yasui and co-workers in 1995.[17] In their study, it was reported that a small amount of arylphosphonate was formed via a phosphonium ion intermediate when arenediazonium salts were reacted with trialkyl phosphites in an alcoholic solvent under an argon atmosphere at 20 °C. Interestingly, according to the report, 4-nitrobenzenediazonium fluoroborate gave a lower yield of arylphosphonate than 4-methylbenzenediazonium fluoroborate, which showed an opposite electronic preference as compared with our phosphorylation reaction. Also, the addition of acetonitrile, which is the best solvent in our phosphorylation reaction, was reported to make the coupling of aryl radical generated from arenediazonium salts with phosphorus species less favorable in Yasui's work. The observation of the opposite results indicates that our phosphorylation reaction may proceed through a different pathway. To gain insights into the mechanistic details of our transformation, the reaction of **1a** in the presence of radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was carried out (Scheme 6). When 10 mol % of TEMPO was

Scheme 6. Radical Trapping Experiments



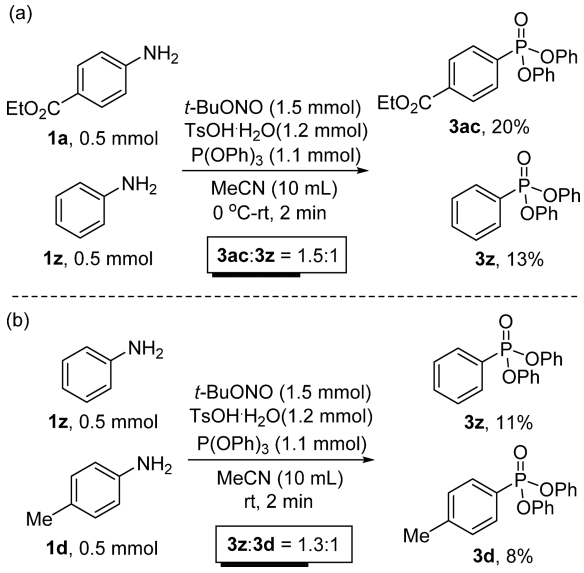
TEMPO	yield
0 mol%	94%
10 mol%	83%
100 mol%	*trace*
150 mol%	*trace*

added, the yield of **3ac** dropped from 94 to 83%. Moreover, the reaction was almost blocked completely when 100 or 150 mol % of TEMPO was added. These results indicate the possibility that a radical process may be involved in this transformation.

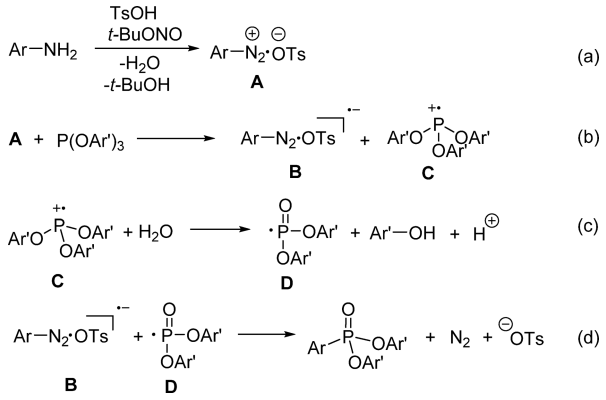
Furthermore, experiments were carried out to reveal the influence of electronic effects of the reaction. Thus, a 1:1 mixture of electron-withdrawing group-substituted aniline **1a** and aniline **1z** was reacted under the optimized conditions, and the reaction was stopped in 2 min to keep the reaction at low conversion of aryl amines. A 1.5:1 ratio of **3ac** and **3z** was observed (Scheme 7a), indicating that electron-deficient **1a** was more reactive. A 1.3:1 ratio of **3z** and **3d** was observed in the similar competition experiment of **1z** and methyl-substituted aniline **1d** (Scheme 7b). The electronic preferences suggest that the decrease of positive charge on the active center occurs during the transformation, which is in accordance with the generation of a radical species from a cationic intermediate.

On the basis of the general understanding of the Sandmeyer-type reaction[18] and our previous mechanistic investigation on Sandmeyer-type borylation and stannylation,[14] we have proposed a mechanism as shown in Scheme 8. First, arylamine reacts with *t*-BuONO to generate diazonium salt intermediate **A**. Then, single electron transfer (SET) between **A** and triphenyl phosphite generates radical anion species **B** and radical cation species **C**. Subsequently, phosphorus radical **D** is formed from **C**, followed by the reaction with **B** to afford the final phosphorylation product along with the release of nitrogen.

Scheme 7. Studies on Electronic Effects



Scheme 8. Proposed Reaction Mechanism



CONCLUSIONS

In summary, we have developed a Sandmeyer-type phosphorylation method to synthesize aryl phosphonates from easily available aryl amines. This metal-free transformation can be conducted under mild conditions without the exclusion of moisture or air. The reaction tolerates a wide range of functional groups and affords the phosphorylation products in moderate to good yields. In light of the importance of aryl phosphonate compounds, we expect that this novel phosphorylation method will find practical applications in the synthesis of these compounds and will be a supplementary method for the construction of aromatic carbon−phosphorus bonds. A detailed mechanistic study and further expansion of the substrate scope are currently under investigation in our laboratory.

EXPERIMENTAL SECTION

General Methods. $P(OMe)_3$, $P(OEt)_3$, $P(OPh)_3$, and the aniline derivatives were purchased from commercial suppliers and used without further purification. The solvents were all distilled prior to use, and 200−300 mesh silica gels were used for the chromatography. Chemical shifts for ^1H NMR (400 MHz) and ^{13}CNMR (100 MHz) are reported relative to the chemical shift of tetramethylsilane (TMS); chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). For ^{31}P NMR (162 MHz) spectra, 85% phosphoric acid

DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603−11611

(δ = 0) served as the external standard. IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. The substituted triaryl phosphites (**6a**–**d**) were prepared following a literature procedure.[19]

General Procedure for the Phosphorylation Reaction. Arylamine (0.2 mmol) and TsOH·H_2O (46 mg, 0.24 mmol) were added into a 10 mL reaction tube. After the addition of MeCN (1.0 mL), the turbid solution was stirred at 0 °C. *t*-BuONO (31 mg, 0.3 mmol) was then added, and the reaction solution was stirred at 0 °C for 15 min, followed by the addition of $P(OR)_3$ (0.6 mmol), the resulting reaction solution was stirred for 8 h at room temperature (around 25 °C). The solution was then concentrated under reduced pressure, and the crude residue was purified by silica gel column chromatography to afford the pure products.

General Procedure for Gram Scale Phosphorylation Reaction. Arylamine (**1a**, **1d**, or **1i**; 20 mmol) and TsOH·H_2O (4.56 g, 24 mmol) were added to a 200 mL reaction bulb. After the addition of MeCN (40 mL), the turbid solution was stirred at 0 °C. *t*-BuONO (3.09 g, 30 mmol) was then added dropwise, and the reaction solution was stirred at 0 °C for 15 min, followed by the addition of $P(OPh)_3$ (18.06 g, 60 mmol). The resulting reaction solution was stirred for 8 h at room temperature (25 °C). The solution was then concentrated under reduced pressure, and the crude residue was purified by silica gel column chromatography to afford the pure product.

The Ester Exchange Experiment.[16] The solution of sodium (130 mg, 5.7 mmol) dissolved in 3.0 mL of ethanol was added to a solution of **3ic** (340 mg, 1.0 mmol) dissolved in 3 mL of ethanol. The reaction solution was stirred at room temperature for 2 h. Then, the mixture was transferred into a 125 mL separating funnel, and 40 mL of diethyl ether was added. The solution was washed by 1 M NaOH (40 mL), and then the water phase was extracted with 20 mL of diethyl ether. The organic phase was then washed by brine (30 mL). After drying by Na_2SO_4 and evaporation, product **3ib** was obtained (215 mg, 88%) as an orange liquid.

3ia was obtained as an orange liquid (205 mg, 84%) by using methanol as solvent under similar conditions. For **3id** (orange liquid, 134 mg, 55%), *i*-PrOH was used instead of ethanol, and the reaction was carried out at 60 °C for 2 h.

The Competition Experiment. Arylamine **1a** (83 mg, 0.5 mmol), **1z** (47 mg, 0.5 mmol), and TsOH·H_2O (228 mg, 1.2 mmol) were added to a 50 mL reaction bulb. After the addition of MeCN (10 mL), the turbid solution was stirred at 0 °C. *t*-BuONO (155 mg, 1.5 mmol) was then added, and the reaction solution was stirred at 0 °C for 15 min, followed by the addition of $P(OPh)_3$ (341 mg, 1.1 mmol). The resulting reaction solution was stirred for 2 min at room temperature (25 °C). The reaction was quenched by filtering the mixture through a short column of silica gel (eluent: ethyl acetate). The solution was then concentrated under reduced pressure, and the crude residue was purified by silica gel column chromatography to afford pure products **3ac** (38 mg, 20%) and **3z** (20 mg, 13%).

*Ethyl 4-(Dimethoxyphosphoryl)benzoate (**3aa**).*[20] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 2:1) afforded **3aa** (28 mg, 54%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.13 (m, 2H), 7.91–7.86 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.79 (d, *J* = 11.1 Hz, 6H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 134.1 (d, *J* = 3.4 Hz), 131.9 (d, *J* = 9.9 Hz), 131.6 (d, *J* = 187.2 Hz), 129.4 (d, *J* = 15.2 Hz), 61.5, 52.9 (d, *J* = 5.6 Hz), 14.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 20.6; IR (film) 1721, 1273, 1104, 1020, 830, 763 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 257 (20), 230 (24), 213 (100), 185 (26), 136 (20), 91 (16); HRMS (ESI) calcd for $C_{11}H_{16}O_5P$ $[M + H]^+$ 259.0730, found 259.0728.

*Ethyl 4-(Diphenoxyphosphoryl)benzoate (**3ac**).*[21] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 5:1) afforded **3ac** (72 mg, 94%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17–8.14 (m, 2H), 8.07–8.01 (m, 2H), 7.31–7.26 (m, 4H), 7.19–7.14 (m, 6H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 150.1 (d, *J* = 7.7 Hz), 134.7 (d, *J* = 3.19 Hz), 132.3 (d, *J* = 10.6 Hz), 131.3 (d, *J* = 192.93 Hz), 129.8, 129.6, 129,5, 120.6 (d, *J* = 4.6 Hz), 61.6, 14.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 10.6; IR (film) 1721, 1489, 1272, 1186, 1103, 932, 762 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 381 (100), 337 (15), 289 (35), 242 (24), 170 (17), 77 (76); HRMS (ESI) calcd for $C_{21}H_{20}O_5P$ $[M + H]^+$ 383.1043, found 383.1043.

*Diphenyl (4-Nitrophenyl)phosphonate (**3b**).*[16] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) afforded **3b** (68 mg, 95%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35–8.32 (m, 2H), 8.19–8.14 (m, 2H), 7.34–7.30 (m, 4H), 7.19–7.18 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.7 (d, *J* = 4.0 Hz), 149.9 (d, *J* = 7.6 Hz), 133.8 (d, *J* = 191.8 Hz), 133.6 (d, *J* = 11.1 Hz), 130.0, 125.7, 123.6 (d, *J* = 16.2 Hz), 120.5 (d, *J* = 4.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 8.2; IR (film) 1589, 1516, 1267, 1187, 945, 932, 777 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 354 (89), 308 (14), 262 (14), 215 (34), 170 (16), 94 (19), 77 (100); HRMS (ESI) calcd for $C_{18}H_{15}NO_5P$ $[M + H]^+$ 356.0682, found 356.0682.

*Diphenyl (4-Cyanophenyl)phosphonate (**3c**).*[16] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) afforded **3c** (66 mg, 98%) as a red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11–8.05 (m, 2H), 7.80–7.77 (m, 2H), 7.33–7.26 (m, 4H), 7.20–7.16 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9 (d, *J* = 7.8 Hz), 132.8 (d, *J* = 10.4 Hz), 132.2 (d, *J* = 15.8 Hz), 132.0 (d, *J* = 192.4 Hz), 130.0, 125.6, 120.5 (d, *J* = 4.6 Hz), 117.6, 116.9 (d, *J* = 3.68 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 8.4; IR (film) 2233, 1590, 1489, 1271, 1185, 935, 767 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 334 (91), 242 (19), 195 (42), 170 (18), 94 (20), 77 (100); HRMS (ESI) calcd for $C_{19}H_{15}NO_3P$ $[M + H]^+$ 336.0784, found 336.0786.

*Diphenyl p-Tolylphosphonate (**3d**).*[16] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3d** (43 mg, 66%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 2H), 7.30–7.25 (m, 6H), 7.19–7.17 (m, 4H), 7.14–7.11 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.4 Hz), 144.0 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 10.9 Hz), 129.7, 129.4 (d, *J* = 16.4 Hz), 125.1, 123.5 (d, *J* = 195.1 Hz), 120.7 (d, *J* = 4.5 Hz), 21.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.48; IR (film) 1592, 1490, 1269, 1188, 1129, 926, 769 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 323 (100), 231 (77), 213 (13), 184 (22), 170 (20), 77 (77); HRMS (ESI) calcd for $C_{19}H_{18}O_3P$ $[M + H]^+$ 325.0988, found 325.0994.

*Diphenyl (4-Chlorophenyl)phosphonate (**3e**).*[16] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 30:1) afforded **3e** (59 mg, 86%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.87 (m, 2H), 7.50–7.47 (m, 2H), 7.35–7.26 (m, 4H), 7.21–7.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2 (d, *J* = 7.5 Hz), 140.0 (d, *J* = 4.2 Hz), 133.7 (d, *J* = 11.4 Hz), 129.8, 129.1 (d, *J* = 16.6 Hz), 125.4 (d, *J* = 195.9 Hz), 125.4, 120.6 (d, *J* = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 11.1; IR (film) 1590, 1489, 1280, 1187, 1088, 930, 772 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 343 (78), 251 (33), 233 (7), 204 (25), 170 (22), 77(100); HRMS (ESI) calcd for $C_{18}H_{15}ClO_3P$ $[M + H]^+$ 345.0442, found 345.0444.

*Diphenyl (4-Bromophenyl)phosphonate (**3f**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 30:1) afforded **3f** (60 mg, 77%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.79 (m, 2H), 7.65–7.62 (m, 2H), 7.31–7.27 (m, 4H), 7.18–7.13 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2 (d, *J* = 7.6 Hz), 133.8 (d, *J* = 11.2 Hz), 132.1 (d, *J* = 16.4 Hz), 129.8, 128.6 (d, *J* = 4.2 Hz), 125.9 (d, *J* = 195.3 Hz), 125.3, 120.6 (d, *J* = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 11.4; IR (film) 1581, 1483, 1266, 1186, 1162, 930, 771 cm^{-1}; EI-MS (*m*/*z*, relative intensity) 389 (63), 295 (29), 248 (16), 170 (21), 77 (100), 51 (16); HRMS (ESI) calcd for $C_{18}H_{15}BrO_3P$ $[M + H]^+$ 388.9937, found 388.9939.

*Diphenyl [1,1′-Biphenyl]-4-ylphosphonate (**3g**).*[22] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3g** (39 mg, 51%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–8.00 (m, 2H), 7.73–7.70 (m, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.49–7.45 (m, 2H), 7.42–7.39 (m, 1H), 7.32–7.29 (m, 4H), 7.23–7.21 (m, 4H), 7.17–7.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, *J* = 7.6 Hz), 146.0 (d, *J* = 3.4 Hz), 139.7, 132.8 (d, *J* = 10.8 Hz), 129.8, 129.0, 128.4, 127.3, 127.3 (d, *J* = 16.1 Hz), 125.3 (*J* = 194.7 Hz), 125.2, 120.7 (d, *J* = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.6; IR (film) 1591, 1488, 1274, 1188, 1133, 928, 761 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{20}O_3P$ $[M + H]^+$ 387.1145, found 387.1146.

DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603–11611

*Diphenyl (4-(Methylthio)phenyl)phosphonate (**3h**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3h** (37 mg, 52%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.80 (m, 2H), 7.30−7.26 (m, 6H), 7.19−7.12(m, 6H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, J = 7.5 Hz), 146.2 (d, J = 3.6 Hz), 132.5 (d, J = 11.1 Hz), 129.8, 125.2, 125.1 (d, J = 16.1 Hz), 122.0 (d, J = 197.5 Hz), 120.6 (d, J = 4.7 Hz), 14.6; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.7; IR (film) 1589, 1489, 1278, 1187, 1085, 927, 773 cm^{-1}; EI-MS (m/z, relative intensity) 356 (100), 263 (94), 216 (23), 170 (12), 139 (9), 77 (68); HRMS (ESI) calcd for $C_{19}H_{18}O_3PS$ [M + H]$^+$ 357.0709, found 357.0708.

*Dimethyl (4-Methoxyphenyl)phosphonate (**3ia**).*[10] Orange liquid (205 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 12.7, 8.7 Hz, 2H), 6.98 (dd, J = 8.7, 3.3 Hz, 2H), 3.85 (s, 3H), 3.74 (d, J = 11.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, J = 3.5 Hz), 133.9 (d, J = 11.2 Hz), 117.9 (d, J = 196.1 Hz), 114.1 (d, J = 16.1 Hz), 55.3, 52.5 (d, J = 5.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 23.1; IR (film) 2955, 1600, 1507, 1244, 1132, 1024, 812 cm^{-1}; EI-MS (m/z, relative intensity) 77 (15), 108 (30), 121 (69), 171 (80), 185 (24), 216 (100).

*Diethyl (4-Methoxyphenyl)phosphonate (**3ib**).*[16] Orange liquid (215 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.72 (m, 2H), 6.98−6.95 (m, 2H), 4.17−4.00 (m, 4H), 3.85 (s, 3H), 1.31 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (d, J = 3.3 Hz), 133.7 (d, J = 11.3 Hz), 119.5 (d, J = 195.0 Hz), 114.0 (d, J = 16.1 Hz), 61.9 (d, J = 5.3 Hz), 55.3, 16.3 (d, J = 6.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 20.3; IR (film) 1600, 1243, 1132, 1022, 962, 807 cm^{-1}; EI-MS (m/z, relative intensity) 244 (39), 216 (43), 188 (100), 171 (54), 135 (24), 108 (59); HRMS (ESI) calcd for $C_{11}H_{18}O_4P$ [M + H]$^+$ 245.0937, found 245.0930.

*Diphenyl (4-Methoxyphenyl)phosphonate (**3ic**).*[16] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) afforded **3ic** (27 mg, 40%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 13.4, 8.8 Hz, 2H), 7.30−7.26 (m, 4H), 7.19−7.11 (m, 6H), 6.98 (dd, J = 8.8, 3.8 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5 (d, J = 3.6 Hz), 150.5 (d, J = 7.4 Hz), 134.4 (d, J = 11.9 Hz), 129.7, 125.0, 120.7 (d, J = 4.5 Hz), 117.8 (d, J = 200.4 Hz), 114.2 (d, J = 16.9 Hz), 55.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 13.3; IR (film) 1597, 1489, 1257, 1187, 1130, 926, 770 cm^{-1}; EI-MS (m/z, relative intensity) 339 (72), 247 (100), 229 (8), 200 (16), 170 (18), 77 (67); HRMS (ESI) calcd for $C_{19}H_{18}O_4P$ [M + H]$^+$ 341.0937, found 341.0943.

*Diisopropyl (4-Methoxyphenyl)phosphonate (**3id**).*[10] Orange liquid (134 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 12.5, 8.6 Hz, 2H), 8.96−8.94 (m, 2H), 4.69−4.61 (m, 2H), 3.84 (s, 3H), 1.36 (d, J = 6.0 Hz, 6H), 1.21 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J = 3.2 Hz), 133.7 (d, J = 11.4 Hz), 121.2 (d, J = 195.3 Hz), 113.8 (d, J = 16.1 Hz), 70.4 (d, J = 5.3 Hz), 55.3, 23.9 (dd, J = 24.1, 3.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 18.0; IR (film) 2979, 2923, 1601, 1242, 1133, 1016, 979 cm^{-1}; EI-MS (m/z, relative intensity) 77 (14), 108 (37), 171 (55), 188 (100), 230 (24), 272 (16).

*Diphenyl (4-Acetylphenyl)phosphonate (**3j**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 5:1) afforded **3j** (62 mg, 89%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08−8.05 (m, 4H), 7.32−7.28 (m, 4H), 7.19−7.16 (m, 6H), 2.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 150.1 (d, J = 7.5 Hz), 140.4 (d, J = 3.1 Hz), 132.7 (d, J = 10.4 Hz), 131.6 (d, J = 191.0 Hz), 129.8, 128.2 (d, J = 16.0 Hz), 125.4, 120.6 (d, J = 4.6 Hz), 26.8; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 10.5; IR (film) 1691, 1590, 1489, 1263, 1186, 930, 764 cm^{-1}; EI-MS (m/z, relative intensity) 353 (100), 337 (17), 259 (39), 212 (17), 170 (15), 77 (94); HRMS (ESI) calcd for $C_{20}H_{18}O_4P$ [M + H]$^+$ 353.0937, found 353.0939.

*Diphenyl o-Tolylphosphonate (**3k**).*[16] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 30:1) afforded **3k** (45 mg, 69%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 15.2, 7.6 Hz, 1H), 7.52−7.28 (m, 1H), 7.34−7.27 (m, 6H), 7.23−7.12 (m, 6H), 2.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3 (d, J = 7.9 Hz), 141.1 (d, J = 10.7 Hz), 133.5 (d, J = 11.1 Hz), 132.3 (d, J = 3.1 Hz), 130.5 (d, J = 15.9 Hz), 128.7, 124.7 (d, J = 15.8 Hz), 124.5 (d, J = 188.7 Hz), 124.1, 119.4 (d, J = 4.7 Hz), 20.5 (d, J = 3.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 13.1; IR (film) 1593, 1490, 1187, 1163, 1025, 928, 757 cm^{-1}; EI-MS (m/z, relative intensity) 324 (100), 288 (19), 231 (22), 212 (29), 165 (22), 94 (27), 77 (72); HRMS (ESI) calcd for $C_{19}H_{18}O_3P$ [M + H]$^+$ 325.0988, found 325.0988.

*Diphenyl (2-Cyanophenyl)phosphonate (**3l**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 5:1) afforded **3l** (58 mg, 87%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30−8.24 (m, 1H), 7.91−7.87 (m, 1H), 7.74−7.71 (m, 2H), 7.33−7.28 (m, 8H), 7.20−7.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0 (d, J = 8.0 Hz), 135.7 (d, J = 9.4 Hz), 134.8 (d, J = 11.6 Hz), 133.4 (d, J = 2.6 Hz), 132.5 (d, J = 14.8 Hz), 129.9 (d, J = 192.9 Hz), 129.9, 125.6, 120.6 (d, J = 4.6 Hz), 117.0 (d, J = 5.9 Hz), 114.9 (d, J = 4.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 6.1; IR (film) 2231, 1589, 1489, 1278, 1184, 944, 764 cm^{-1}; EI-MS (m/z, relative intensity) 335 (100), 242 (39), 224 (22), 195 (62), 170 (20), 77 (97); HRMS (ESI) calcd for $C_{19}H_{15}NO_3P$ [M + H]$^+$ 336.0784, found 336.0787.

*Diphenyl (2-Chlorophenyl)phosphonate (**3m**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 30:1) afforded **3m** (55 mg, 80%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.11 (m, 1H), 7.54−7.50 (m, 2H), 7.39−7.32 (m, 1H), 7.31−7.23 (m, 8H), 7.16−7.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2 (d, J = 7.4 Hz), 137.0, 136.9 (d, J = 8.8 Hz), 134.6, 131.1 (d, J = 10.6 Hz), 129.8, 126.7 (d, J = 14.7 Hz), 125.9 (d, J = 196.4 Hz), 125.3, 120.6 (d, J = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 8.2; IR (film) 1587, 1489, 1268, 1186, 1052, 940, 757 cm^{-1}; EI-MS (m/z, relative intensity) 344 (100), 309 (71), 251 (21), 215 (83), 168 (37), 77 (88); HRMS (ESI) calcd for $C_{18}H_{15}ClO_3P$ [M + H]$^+$ 345.0442, found 345.0441.

*Diphenyl (3-Nitrophenyl)phosphonate (**3n**).*[23] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3n** (59 mg, 69%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 13.3 Hz, 1H), 8.46 (d, J = 8.3 Hz, 1H), 8.29 (dd, J = 13.2, 7.6 Hz, 1H), 7.76−7.70 (m, 1H), 7.34−7.30 (m, 4H), 7.21−7.17 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9 (d, J = 7.9 Hz), 148.1 (d, J = 19.1 Hz), 138.0 (d, J = 10.3 Hz), 130.1 (d, J = 16.5 Hz), 130.0, 129.5 (d, J = 196.5 Hz), 127.8 (d, J = 2.9 Hz), 127.2 (d, J = 12.1 Hz), 125.7, 120.5 (d, J = 4.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 8.1; IR (film) 1590, 1532, 1489, 1362, 1185, 936, 762 cm^{-1}; EI-MS (m/z, relative intensity) 355 (100), 338 (17), 308 (308 (47), 170 (25), 94 (17), 77 (89); HRMS (ESI) calcd for $C_{18}H_{15}NO_5P$ [M + H]$^+$ 356.0682, found 356.0685.

*Diphenyl (3-Acetamidophenyl)phosphonate (**3o**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 2:1) afforded **3o** (31 mg, 42%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.41 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 15.9 Hz, 1H), 7.59 (dd, J = 13.4, 7.6 Hz, 1H), 7.48−7.43 (m, 1H), 7.26−7.21 (m, 4H), 7.14−7.10 (m, 6H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 150.0 (d, J = 7.7 Hz), 139.7 (d, J = 20.2 Hz), 129.8, 129.6, 126.3 (d, J = 194.0 Hz), 126.2 (d, J = 8.6 Hz), 125.5, 124.5 (d, J = 3.0 Hz), 123.2 (d, J = 13.6 Hz), 120.7 (d, J = 4.3 Hz), 24.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.8; IR (film) 3295, 2926, 1549, 1488, 1185, 935, 771 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{19}NO_4P$ [M + H]$^+$ 368.1046, found 368.1051.

*3-(Diphenoxyphosphoryl)phenyl Acetate (**3p**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) afforded **3p** (59 mg, 81%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 13.6, 7.6 Hz, 1H), 7.72 (d, J = 15.1 Hz, 1H), 7.54−7.49 (m, 1H), 7.36−2.28 (m, 5H), 7.19−7.13 (m, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 150.7 (d, J = 21.3 Hz), 150.2 (d, J = 7.8 Hz), 130.0 (d, J = 18.1 Hz), 129.8, 129.6 (d, J = 9.8 Hz), 128.6 (d, J = 194.5 Hz), 126.7 (d, J = 3.4 Hz), 125.4 (d, J = 11.1 Hz), 125.3, 120.6 (d, J = 4.5 Hz), 21.1; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 10.6; IR (film) 1770, 1590, 1489, 1277, 1187, 933, 771 cm^{-1}; EI-MS (m/z, relative intensity) 368 (14), 326 (100), 233 (14), 186 (7), 170 (9), 94 (6), 77 (29); HRMS (ESI) calcd for $C_{20}H_{18}O_5P$ [M + H]$^+$ 369.0886, found 369.0889.

*Diphenyl (3-Bromophenyl)phosphonate (**3q**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 30:1) afforded **3q** (67 mg, 86%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 14.3 Hz, 1H), 7.89 (dd, J = 13.6, 7.6 Hz, 1H), 7.74- 7.32 (m, 1H), 7.41−7.37 (m, 1H), 7.33−7.29 (m, 4H), 7.19- 7.15 (m, 6H); ^{13}C

DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603−11611

NMR (100 MHz, $CDCl_3$) δ 150.1 (d, J = 7.7 Hz), 136.3 (d, J = 2.9 Hz), 135.0 (d, J = 11.1 Hz), 130.7 (d, J = 9.7 Hz), 130.3 (d, J = 16.9 Hz), 129.9, 129.4 (d, J = 192.7 Hz), 125.4, 123.0 (d, J = 20.7 Hz), 120.6 (d, J = 4.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 9.6; IR (film) 1590, 1488, 1275, 1186, 1137, 932, 763 cm^{-1}; EI-MS (m/z, relative intensity) 389 (56), 310 (16), 295 (24), 248 (16), 170 (28), 77 (100); HRMS (ESI) calcd for $C_{18}H_{15}BrO_3P$ $[M + H]^+$ 388.9937, found 388.9936.

*Diphenyl (4-((Triisopropylsilyl)ethynyl)phenyl)phosphonate (**3ra**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 50:1) afforded **3ra** (64 mg, 65%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 13.8, 8.1 Hz, 2H), 7.59−7.56 (m, 2H), 7.31−7.27 (m, 4H), 7.18−7.13 (m, 6H), 1.13 (s, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2 (d, J = 7.3 Hz), 132.2 (d, J = 6.6 Hz), 132.0 (d, J = 12.2 Hz), 129.8, 128.5 (d, J = 3.7 Hz), 126.3 (d, J = 193.4 Hz), 125.3, 120.6 (d, J = 4.6 Hz), 105.7, 95.0, 18.6, 11.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 11.5; IR (film) 2943, 2866, 1596, 1490, 1187, 1127, 932 cm^{-1}; EI-MS (m/z, relative intensity) 490 (3), 447 (100), 419 (24), 405 (26), 391 (33), 377 (44), 77 (26); HRMS (ESI) calcd for $C_{29}H_{36}O_3PSi$ $[M + H]^+$ 491.2166, found 491.2165.

*Diphenyl (4-Ethynylphenyl)phosphonate (**3rb**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3rb** (32 mg, 48%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.81 (m, 2H), 7.54−7.51 (m, 2H), 7.24−7.18 (m, 4H), 7.11−7.06 (m, 6H), 3.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.2 (d, J = 7.5 Hz), 132.3 (d, J = 2.3 Hz), 132.1 (d, J = 3.0 Hz), 129.8, 127.2 (d, J = 3.7 Hz), 127.2 (d, J = 193.6 Hz), 125.3, 120.6 (d, J = 4.5 Hz), 82.4, 80.5; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 11.1; IR (film) 1593, 1489, 1186, 1125, 930, 767 cm^{-1}; EI-MS (m/z, relative intensity) 333 (100), 241 (60), 223 (16), 194 (46), 170 (20), 77 (97); HRMS (ESI) calcd for $C_{20}H_{16}O_3P$ $[M + H]^+$ 335.0832, found 335.0840.

*Diphenyl Naphthalen-1-ylphosphonate (**3sa**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3sa** (25 mg, 35%) as a red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 8.6 Hz, 1H), 8.40−8.34 (m, 1H), 8.09 (d, J = 8.3 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.74−7.69 (m, 1H), 7.63−7.59 (m, 1H), 7.56−7.51 (m, 1H), 7.31−7.24 (m, 4H), 7.20−7.16 (m, 4H), 7.14−7.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, J = 7.6 Hz), 135.8 (d, J = 10.0 Hz), 134.6 (d, J = 3.6 Hz), 133.6 (d, J = 13.6 Hz), 132.5 (d, J = 11.1 Hz), 129.7, 129.1, 128.0, 126.7, 126.5 (d, J = 4.3 Hz), 125.2, 124.6 (d, J = 17.6 Hz), 123.2 (d, J = 187.8 Hz), 120.6 (d, J = 4.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.7; IR (film) 1591, 1489, 1272, 1187, 996, 928, 774 cm^{-1}; EI-MS (m/z, relative intensity) 360 (99), 267 (100), 249 (42), 202 (26), 173 (26), 127 (28), 77 (59); HRMS (ESI) calcd for $C_{22}H_{18}O_3P$ $[M + H]^+$ 361.0988, found 361.0990.

*Diphenyl Naphthalen-2-ylphosphonate (**3sb**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3sb** (32 mg, 44%) as an orange solid; mp 84−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 16.4 Hz, 1H), 7.95−7.87 (m, 4H), 7.64−7.55 (m, 2H), 7.30−7.21 (m, 8H), 7.14- 7.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, J = 7.5 Hz), 135.3 (d, J = 2.8 Hz), 135.2 (d, J = 11.0 Hz), 132.3 (d, J = 17.7 Hz), 129.8, 129.2, 128.8, 128.6 (d, J = 15.0 Hz), 127.9, 127.2, 126.4 (d, J = 10.2 Hz), 125.2 (d, J = 1.0 Hz), 123.8 (d, J = 193.1 Hz), 120.7 (d, J = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.6; IR (film) 1589, 1489, 1277, 1187, 1085, 926, 771 cm^{-1}; EI-MS (m/z, relative intensity) 360 (100), 267 (73), 220 (22), 204 (21), 170 (11), 127 (28), 77 (67); HRMS (ESI) calcd for $C_{22}H_{18}O_3P$ $[M + H]^+$ 361.0988, found 361.0984.

*Diphenyl (4-Nitronaphthalen-1-yl)phosphonate(**3t**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) afforded **3t** (81 mg, 99%) as a yellow solid; mp 106−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, J = 8.1 Hz, 1H), 8.49−8.40 (m, 2H), 8.05 (dd, J = 7.6, 3.3 Hz, 1H), 7.88−7.80 (m, 2H), 7.31−7.21 (m, 4H), 7.19−7.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1 (d, J = 4.4 Hz), 150.0 (d, J = 7.4 Hz), 134.1 (d, J = 10.0 Hz), 133.9 (d, J = 12.0 Hz), 130.0, 129.6, 129.6 (d, J = 186.5 Hz), 129.3, 127.1 (d, J = 4.3 Hz), 125.6, 124.9 (d, J = 13.9 Hz), 123.6, 120.9, (d, J = 18.0 Hz), 120.4 (d, J = 4.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 9.5; IR (film) 1590, 1257, 1489, 1278, 1184, 937, 766, 689 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{17}NO_5P$ $[M + H]^+$ 406.0839, found 406.0844.

*Diphenyl (3-Fluoro-4-nitrophenyl)phosphonate (**3u**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) afforded **3u** (50 mg, 67%) as a yellow solid; mp 81−84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18−8.13 (m, 1H), 7.94−7.87 (m, 2H), 7.36−7.32 (m, 4H), 7.22−7.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9 (dd, J = 269.0, 22.82 Hz), 149.7 (d, J = 7.8 Hz), 140.2 (dd, J = 4.5, 2.2 Hz), 135.3 (dd, J = 185.9, 6.6 Hz), 130.1, 128.3 (dd, J = 9.5, 5.0 Hz), 126.5 (dd, J = 17.7, 2.7 Hz), 125.9 (d, J = 0.9 Hz), 122.6 (dd, J = 22.2, 11.5 Hz), 120.4 (d, J = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 5.1; IR (film) 1597, 1533, 1489, 1279, 1184, 942, 737 cm^{-1}; EI-MS (m/z, relative intensity) 373 (98), 326 (20), 280 (8), 233 (35), 170 (20), 77 (97); HRMS (ESI) calcd for $C_{18}H_{14}FNO_5P$ $[M + H]^+$ 374.0588, found 374.0592.

*Diphenyl (E)-(4-(Phenyldiazenyl)phenyl)phosphonate (**3v**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 30:1) afforded **3v** (35 mg, 42%) as a red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.09 (m, 2H), 8.01−7.94 (m, 4H), 7.55−7.52 (m, 3H), 7.34−7.28 (m, 4H), 7.23−7.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2 (d, J = 3.9 Hz), 152.5, 150.3 (d, J = 7.5 Hz), 133.4 (d, J = 11.0 Hz), 132.0, 129.8, 129.2, 128.9 (d, J = 202.1 Hz), 125.3, 123.2, 122.8 (d, J = 16.4 Hz), 120.6 (d, J = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 11.0; IR (film) 1593, 1489, 1274, 1187, 1125, 931, 769 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{20}N_2O_3P$ $[M + H]^+$ 415.1206, found 415.1212.

*Ethyl (E)-3-(4-(Diphenoxyphosphoryl)phenyl)acrylate (**3w**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) afforded **3w** (41 mg, 50%) as a red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.95 (m, 2H), 7.70−7.62 (m, 3H), 7.32−7.26 (m, 4H), 7.20−7.14 (m, 6H), 6.53 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 150.2 (d, J = 7.8 Hz), 142.8, 139.0 (d, J = 3.5 Hz), 132.8 (d, J = 10.6 Hz), 129.8, 128.4 (d, J = 193.7 Hz), 128.0 (d, J = 16.1 Hz), 125.3, 121.3, 120.6 (d, J = 4.6 Hz), 60.8, 14.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 11.3; IR (film) 2923, 1713, 1489, 1276, 1184, 936, 771, 681 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}O_5P$ $[M + H]^+$ 409.1199, found 409.1197.

*Diphenyl (3-(Benzyloxy)phenyl)phosphonate (**3x**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3x** (51 mg, 61%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58−7.53 (m, 2H), 7.43−7.34 (m, 6H), 7.31−7.27 (m, 4H), 7.21−7.13 (m, 7H), 5.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6 (d, J = 20.1 Hz), 150.4 (d, J = 7.5 Hz), 136.3, 130.0 (d, J = 18.7 Hz), 129.8, 128.7, 128.2, 128.0 (d, J = 191.9 Hz), 127.6, 125.2, 124.8 (d, J = 9.7 Hz), 120.6 (d, J = 4.5 Hz), 120.5 (d, J = 3.2 Hz), 117.8 (d, J = 12.0 Hz), 70.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.1; IR (film) 1592, 1488, 1230, 1185, 1025, 938, 755 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}O_4P$ $[M + H]^+$ 417.1250, found 417.1248.

*Diphenyl (3,5-Difluorophenyl)phosphonate (**3ya**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 30:1) afforded **3ya** (42 mg, 61%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ7.52−7.46 (m, 2H), 7.34−7.30 (m, 4H), 7.20−7.16 (m, 6H), 7.07−7.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (ddd, J = 253.8, 26.8, 8.9 Hz), 150.0 (d, J = 7.7 Hz), 130.8 (d, J = 196.2 Hz), 129.9, 125.6, 120.5 (d, J = 4.5 Hz), 115.3 (dd, J = 26.6, 10.5 Hz), 108.9 (dt, J = 24.8, 2.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 8.2; IR (film) 1593, 1489, 1430, 1304, 1185, 936, 768 cm^{-1}; EI-MS (m/z, relative intensity) 345 (100), 253 (18), 206 (34), 170 (20), 94 (15), 77 (86); HRMS (ESI) calcd for $C_{18}H_{14}F_2O_3P$ $[M + H]^+$ 347.0643, found 347.0641.

*Diphenyl (3,4-Difluorophenyl)phosphonate (**3yb**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3yb** (56 mg, 81%) as a yellow solid; mp 89−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82−7.70 (m, 2H), 7.32−7.28 (m, 5H), 7.19−7.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (ddd, J = 257.5, 12.5, 3.8 Hz), 150.4 (ddd, J = 253.1, 24.0, 12.7 Hz), 150.1 (d, J = 7.5 Hz), 129.9, 129.6 (ddd, J = 10.3, 7.4, 4.1 Hz), 125.5, 124.1 (dt, J = 198.3, 4.5 Hz), 121.7 (ddd, J = 18.4, 11.9, 1.2 Hz), 120.5 (d, J = 4.5 Hz), 118.3 (t, J = 18.3 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 9.1; IR (film) 1590, 1489, 1278, 1186, 1093, 934, 769 cm^{-1}; EI-MS (m/z, relative intensity) 345 (95), 254 (29), 206 (30), 170 (22), 77 (100), 51 (19);

DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603−11611

HRMS (ESI) calcd for $C_{18}H_{14}F_2O_3P$ $[M + H]^+$ 347.0643, found 347.0647.

*Diphenyl Phenylphosphonate (**3z**).*[16] Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **3z** (49 mg, 79%) as a yellow solid; mp 70−72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.94 (m, 2H), 7.62−7.59 (m, 1H), 7.52−7.49 (m, 2H), 7.31−7.27 (m, 4H), 7.20−7.12 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4 (d, J = 7.5 Hz), 133.2 (d, J = 3.2 Hz), 132.3 (d, J = 10.4 Hz), 129.7, 128.7 (d, J = 15.9 Hz), 126.9 (d, J = 192.8 Hz), 125.1, 120.6 (d, J = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.3; IR (film) 1591, 1489, 1270, 1187, 1131, 926, 773, 689 cm^{-1}; EI-MS (m/z, relative intensity) 309 (100), 217 (43), 199 (11), 170 (34), 152 (8), 77(57); HRMS (ESI) calcd for $C_{18}H_{16}O_3P$ $[M + H]^+$ 311.0832, found 311.0827.

*Ethyl 5-(Diphenoxyphosphoryl)benzofuran-2-carboxylate (**5a**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 5:1) afforded **5a** (49 mg, 58%) as an orange liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 14.63 Hz, 1H), 8.06−8.00 (m, 1H), 7.74−7.70 (m, 1H), 7.58 (s, 1H), 7.31−7.26 (m, 4H), 7.20−7.13 (m, 6H), 4.46 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 157.8, 150.3 (d, J = 7.5 Hz), 147.3, 130.7 (d, J = 12.2 Hz), 129.8, 128.8 (d, J = 12.1 Hz), 127.2 (d, J = 10.0 Hz), 125.3, 122.4 (d, J = 195.5 Hz), 120.6 (d, J = 4.5 Hz), 113.6, 113.1 (d, J = 16.9 Hz), 61.9, 14.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.3; IR (film) 1728, 1590, 1489, 1186, 1087, 932, 767 cm^{-1}; EI-MS (m/z, relative intensity) 421 (100), 377 (9), 329 (58), 207 (11), 170 (12), 77 (60); HRMS (ESI) calcd for $C_{23}H_{20}O_6P$ $[M + H]^+$ 423.0992, found 423.0996.

*Diphenyl (5-Bromopyridin-3-yl)phosphonate (**5b**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 15:1) afforded **5b** (21 mg, 27%) as a white solid; mp 138−141 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (d, J = 5.6 Hz, 1H), 8.88 (s, 1H), 8.31 (d, J = 14.2 Hz, 1H), 7.35−7.31 (m, 4H), 7.20−7.18 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 150.5 (d, J = 11.8 Hz), 149.8 (d, J = 7.7 Hz), 142.1 (d, J = 9.1 Hz), 130.0, 125.7, 125.3 (d, J = 191.7 Hz), 121.1 (d, J = 14.9 Hz), 120.5 (d, J = 4.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 6.8; IR (film) 1589, 1488, 1265, 1185, 1160, 943, 770 cm^{-1}; EI-MS (m/z, relative intensity) 389 (56), 310 (31), 296 (36), 251 (8), 170 (16), 77 (100); HRMS (ESI) calcd for $C_{17}H_{14}BrNO_3P$ $[M + H]^+$ 389.9889, found 389.9892.

*Diphenyl (6-Methoxypyridin-3-yl)phosphonate (**5c**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 10:1) afforded **5c** (17 mg, 25%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (dd, J = 7.0, 1.9 Hz, 1H), 8.02 (ddd, J = 12.2, 8.6, 2.2 Hz, 1H), 7.33−7.29 (m, 4H), 7.21−7.14 (m, 6H), 6.82 (dd, J = 8.6, 2.9 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 152.4 (d, J = 15.4 Hz), 150.2 (d, J = 7.5 Hz), 141.7 (d, J = 10.4 Hz), 129.8, 125.3, 120.6 (d, J = 4.7 Hz), 115.3 (d, J = 201.5 Hz), 111.3 (d, J = 13.3 Hz), 54.0; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 11.2; IR (film) 1592, 1488, 1275, 1187, 1024, 929, 770, 689 cm^{-1}; EI-MS (m/z, relative intensity) 340 (100), 325 (9), 248 (75), 207 (12), 170 (14), 77 (46); HRMS (ESI) calcd for $C_{18}H_{17}NO_4P$ $[M + H]^+$ 342.0890, found 342.0893.

*Diphenyl (6-(Trifluoromethyl)pyridin-3-yl)phosphonate (**5d**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 15:1) afforded **5d** (47 mg, 63%) as a white solid; mp 129−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, J = 5.7 Hz, 1H), 8.37 (dd, J = 13.4, 8.1 Hz, 1H), 7.75 (dd, J = 7.8, 2.5 Hz, 1H), 7.28−7.24 (m, 4H), 7.13−7.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7 (d, J = 12.9 Hz), 149.7 (d, J = 7.7 Hz), 141.9 (d, J = 9.4 Hz), 130.1, 127.0 (d, J = 193.2 Hz), 125.8, 120.9 (q, J = 276.6 Hz), 120.4 (d, J = 4.7 Hz), 120.3 (d, J = 9.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ 6.6; IR (film) 2928, 1590, 1485, 1335, 1184, 1160, 1078, 945 cm^{-1}; EI-MS (m/z, relative intensity) 378 (100), 286 (33), 239 (20), 170 (12), 94 (9), 77 (68); HRMS (ESI) calcd for $C_{18}H_{14}F_3NO_3P$ $[M + H]^+$ 380.0658, found 380.0658.

*Diphenyl (2-Methylbenzo[d]thiazol-5-yl)phosphonate (**5e**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 5:1) afforded **5e** (23 mg, 30%) as an orange solid; mp 102−105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, J = 15.3 Hz, 1H), 7.97−7.88 (m, 2H), 7.30−7.26 (m, 4H), 7.22−7.18 (m, 4H), 7.16−7.12 (m, 2H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 153.0 (d, J = 21.1 Hz), 150.3 (d, J = 7.6 Hz), 141.1, 129.8, 127.5 (d, J = 11.7 Hz), 126.8 (d, J = 11.1 Hz), 125.2, 124.4 (d, J = 195.0 Hz), 122.0 (d. J = 18.1 Hz), 120.6 (d, J = 4.6 Hz), 20.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 12.1; IR (film) 1592, 1489, 1274, 1187, 1059, 931, 772, 689 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{17}NO_3PS$ $[M + H]^+$ 382.0661, found 382.0663.

*Ethyl 4-(Bis(4-chlorophenoxy)phosphoryl)benzoate (**7a**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 15:1) afforded **7a** (66 mg, 73%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19−8.16 (m, 2H), 8.04−7.99 (m, 2H), 7.27−7.55 (m, 4H), 7.13−7.11 (m, 4H), 4.42 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 148.5 (d, J = 7.6 Hz), 135.0 (d, J = 3.5 Hz), 132.3 (d, J = 10.8 Hz), 131.0, 130.4 (d, J = 191.1 Hz), 129.9, 129.7 (d, J = 15.96 Hz), 121.9 (d, J = 4.6 Hz), 61.7, 14.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 11.2; IR (film) 1724, 1486, 1273, 1192, 1102, 926 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{18}Cl_2O_5P$ $[M + H]^+$ 451.0263, found 451.0258.

*Ethyl 4-(Bis(4-bromophenoxy)phosphoryl)benzoate (**7b**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 30:1) afforded **7b** (80 mg, 74%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19−8.16 (m, 2H), 8.04−7.98 (m, 2H), 7.42−7.40 (m, 4H), 7.08−7.05 (m, 4H), 4.42 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 149.0 (d, J = 7.4 Hz), 135.1 (d, J = 3.3 Hz), 132.9, 132.3 (d, J = 10.7 Hz), 130.3 (d, J = 191.0 Hz), 129.7 (d, J = 16.0 Hz), 122.3 (d, J = 4.7 Hz), 118.6, 61.7, 14.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 10.8; IR (film) 1721, 1482, 1273, 1191, 1012, 926, 830, 759 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{18}Br_2O_5P$ $[M + H]^+$ 538.9253, found 538.9248.

*Ethyl 4-(Bis(4-methoxyphenoxy)phosphoryl)benzoate (**7c**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 20:1) afforded **7c** (45 mg, 51%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.14 (m, 2H), 8.07−8.01 (m, 2H), 7.20−7.16 (m, 2H), 6.80−6.69 (m, 6H), 4.41 (q, J = 7.1 Hz, 2H), 3.74 (s, 6H), 1.41 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 160.7, 151.0 (d, J = 7.6 Hz), 134.6 (d, J = 3.3 Hz), 132.3 (d, J = 10.5 Hz), 131.3 (d, J = 191.6 Hz), 129.5 (d, J = 15.7 Hz), 112.6 (d, J = 4.4 Hz), 111.3, 61.6, 55.4, 14.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 10.1; IR (film) 1722, 1607, 1490, 1270, 1133, 961, 858 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}O_7P$ $[M + H]^+$ 443.1254, found 443.1263.

*Ethyl 4-(Bis(4-(tert-butyl)phenoxy)phosphoryl)benzoate (**7d**).* Flash chromatography (silica gel, petroleum ether:ethyl acetate = 50:1) afforded **7d** (88 mg, 89%) as a pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.14 (m, 2H), 8.08−8.02 (m, 2H), 7.30−7.28 (m, 4H), 7.10−7.08 (m, 4H), 4.41 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H), 1.27 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 148.2, 147.8 (d, J = 7.6 Hz), 134.5 (d, J = 3.2 Hz), 132.4 (d, J = 10.5 Hz), 131.7 (d, J = 191.1 Hz), 129.5 (d, J = 15.7 Hz), 126.7, 119.9 (d, J = 4.4 Hz), 61.6, 34.4, 31.4, 14.3; ^{31}P NMR ($CDCl_3$, 162 MHz) δ 10.8; IR (film) 2963, 1724, 1508, 1272, 1169, 947 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{36}O_5P$ $[M + H]^+$ 495.2295, found 495.2310.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01820.

Copies of ^{1}H and ^{13}C spectra for all of the products (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to National Basic Research Program of China (973 Program, No. 2015CB856600) and Natural Science

DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603−11611

Foundation of China (Grant 21472004 and 21332002) for the financial support.

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DOI: 10.1021/acs.joc.6b01820
J. Org. Chem. 2016, 81, 11603−11611