JOC The Journal of Organic Chemistry

pubs.acs.org/joc Note

Direct Synthesis of *ortho*-Halogenated Arylphosphonates via a Three-Component Reaction Involving Arynes

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Cite This: *J. Org. Chem.* 2021, 86, 7010–7018 Read Online

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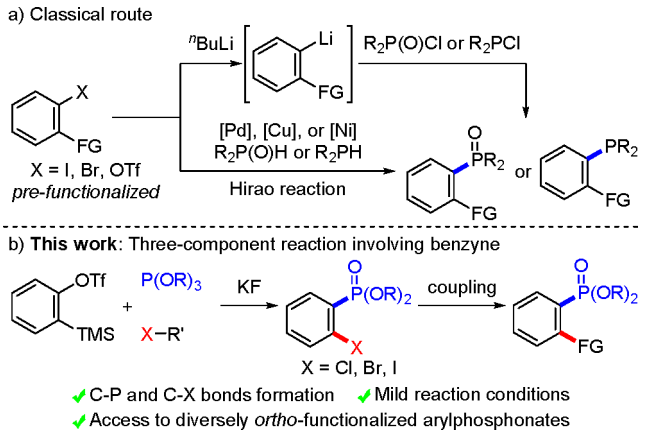
ABSTRACT: A three-component reaction involving arynes, trialkyl phosphites, and halides has been achieved under mild reaction conditions. This transformation provides a direct synthetic approach to *ortho*-halogenated arylphosphonates, which could be rapidly converted to diversely *ortho*-functionalized arylphosphorus compounds.

Arylphosphorus compounds are of great importance for organic synthesis,[1] material chemistry,[2] and medicinal chemistry.[3] In particular, *ortho*-substituents on the phenyl ring are useful fragments for phosphine ligands and other applications.[4] For example, dialkylbiaryl phosphines are known as Buchwald-type phosphine ligands, which become air stable due to the presence of sterically hindered *ortho*-substituents.[5] These arylphosphorus compounds can typically be synthesized via the addition of *n*-butyllithium to *ortho*-functionalized aryl halides followed by quenching with phosphorus electrophiles (Scheme 1a, up).[6] An alternative

Scheme 1. Synthesis of *ortho*-Functionalized Arylphosphorus Compounds



method employs Pd-, Cu-, or Ni-catalyzed Hirao reaction of these aryl halides with phosphorus nucleophiles (Scheme 1a, down).[7] Noteworthily, the direct *ortho*-functionalization of arylphosphorus compounds using the strategy of transition-metal-catalyzed aryl C−H activation has been well-documented over the past decade.[8] However, previous methods are often limited by the availability of the starting materials. In addition, strong bases, transition-metal catalysts, expensive ligands, high temperatures, or long reaction times are generally required for the reaction conditions. Thus, the development of a mild and efficient synthetic protocol for the preparation of *ortho*-functionalized arylphosphorus compounds is highly desirable.

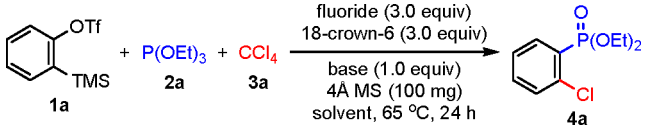
Arynes including benzyne have been of particular interest due to their high reactivity and broad applications in organic synthesis.[9,10] Notably, aryne chemistry has been widely utilized in constructing aryl C−P bonds under mild reaction conditions, providing various arylphosphorus compounds with good efficiency.[11] Three-component reactions involving arynes, which mainly include the initial addition of nucleophiles to arynes and subsequent trapping of the aryl anion intermediate with electrophiles, enable the rapid assembly of 1,2-disubstituted arenes with ample structural diversification.[9,12] However, three-component reactions of arynes, phosphorus nucleophiles, and other electrophiles have received less attention, and the employment of phosphorus nucleophiles and the electrophilic components is limited to tertiary phosphines and carbonyl compounds.[13] It is noteworthy that Wittig and co-workers have reported a series of work on the *ortho*-difunctionalization reaction of arynes and organophosphorus compounds.[14] With the above background and our recent studies on phosphorylation reactions,[15] we became interested in developing a novel three-component reaction of arynes, phosphorus nucleophiles, and halogen electrophiles[12a−e] for accessing *ortho*-halogenated arylphosphorus compounds, which could be rapidly converted to diversely *ortho*-functionalized arylphosphorus compounds.[1b−e] To the best of our knowledge, this type of reaction has never

Received: March 8, 2021
Published: April 21, 2021

been reported. Herein, we describe a direct approach for the synthesis of *ortho*-halogenated arylphosphonates through a three-component reaction of silylaryl triflates as aryne precursors,[16] trialkyl phosphites, and halides under mild reaction conditions (Scheme 1b).

According to our recent studies on P-arylation of dialkyl phosphites and secondary phosphine oxides with arynes,[15a,b] we first examined the three-component reaction of commercially available benzyne precursor **1a**, diethyl phosphite or diphenylphosphine oxide (3.0 equiv), and CCl_4 (15 equiv) in the presence of CsF (3.0 equiv) and 4 Å molecular sieves in anhydrous CH_3CN at 65 °C. Unfortunately, only the direct P-arylation products formed by the protonation of the aryl anion intermediates[15a] were observed probably due to the acidic hydrogen atoms of $R_2P(O)H$. Inspired by Mhaske's pioneering research,[17] triethyl phosphite **2a** containing no acidic hydrogen atoms was then employed as the phosphorus nucleophile, and a range of reaction conditions were investigated as shown in Table 1. To our delight, the reaction afforded the desired

Table 1. Optimization of the Reaction Conditions[a]



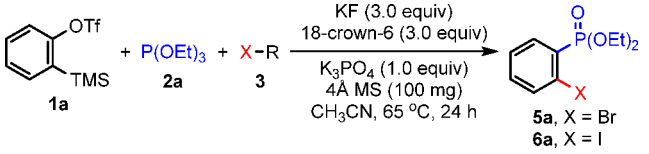
entry	fluoride	base	solvent	yield of **4a** (%)
1[b]	CsF		CH_3CN	27
2	CsF		CH_3CN	39
3	KF		CH_3CN	45
4	KF		THF	33
5	KF		DCE	30
6	KF	Cs_2CO_3	CH_3CN	27
7	KF	K_2CO_3	CH_3CN	32
8	KF	K_3PO_4	CH_3CN	56
9[c]	KF	K_3PO_4	CH_3CN	76
10[d]	KF	K_3PO_4	CH_3CN	80
11[d,e]	KF	K_3PO_4	CH_3CN	48
12[d,f]	KF	K_3PO_4	CH_3CN	0

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), **3a** (3 mmol), fluoride (0.6 mmol), 18-crown-6 (0.6 mmol), base (0.2 mmol), 4 Å MS (100 mg), solvent (2 mL), 65 °C, 24 h. Isolated yield. [b]The reaction was performed without 18-crown-6. [c]0.3 mmol of **1a** and 0.2 mmol of **2a** were employed. [d]0.4 mmol of **1a** and 0.2 mmol of **2a** were employed. [e]The reaction was performed at 80 °C. [f]The reaction was performed at 40 °C.

diethyl *ortho*-chlorophenylphosphonate **4a** in 27% isolated yield (entry 1), together with the protonated product diethyl phenylphosphonate[17] in 40% yield. With the use of 18-crown-6 (3.0 equiv) and KF instead of CsF, the desired **4a** was isolated in 45% yield (entries 2 and 3). A simple screening of solvents was then carried out (entries 4 and 5), and CH_3CN was proved to be the optimum solvent. When an inorganic base was introduced into the reaction (entries 6−8), the yield of **4a** increased to 56% in the presence of K_3PO_4 probably due to the neutralization of HCl generated by CCl_4 or other acidic protons with bases (entry 8). Pleasingly, when the reaction was carried out with excess amounts of benzyne precursor **1a** (1.5 or 2.0 equiv), the yield of **4a** significantly increased to 76% (entry 9) or 80% (entry 10). It is noteworthy that only trace amounts of the protonated product were detected in the reaction (entry 10). The product yield significantly decreased when the reaction was performed at 80 or 40 °C (entries 11 and 12). In addition, the reaction using $CHCl_3$ or NCS instead of CCl_4 as the chlorine source failed to give the corresponding **4a**.

Aryl iodides or bromides are typically employed for the transition-metal-catalyzed cross-coupling reactions, while aryl chlorides are usually unreactive under mild reaction conditions.[1b−e] We then turned to screening of halogen sources to prepare other halogenated arylphosphonates. As shown in Table 2, the employment of CBr_4, NBS, CCl_3Br, or CBr_3F

Table 2. Screening of Halogen Sources[a]



entry	**3** (equiv)	product (yield)
1[b]	CBr_4 (3)	**5a** (0%)
2	NBS (3)	**5a** (0%)
3	CCl_3Br (15)	**5a** (0%)
4	CBr_3F (15)	**5a** (0%)
5[b]	$CHBr_3$ (15)	**5a** (62%)
6[b]	CHI_3 (3)	**6a** (35%)
7	NIS (3)	**6a** (0%)
8	I_2 (3)	**6a** (0%)

[a]Reaction conditions: **1a** (0.4 mmol), **2a** (0.2 mmol), **3** (3 or 15 equiv), KF (0.6 mmol), 18-crown-6 (0.6 mmol), K_3PO_4 (0.2 mmol), 4 Å MS (100 mg), CH_3CN (2 mL), 65 °C, 24 h. Isolated yield based on **2a**. [b]K_3PO_4 was replaced by DBU.

failed to give the desired *ortho*-bromophenylphosphonate **5a** (entries 1−4), while the use of $CHBr_3$ as the bromine source smoothly afforded **5a** in 62% yield in the presence of DBU instead of K_3PO_4 (entry 5). Similarly, *ortho*-iodophenylphosphonate **6a** was obtained in 35% yield with the use of CHI_3 as the iodine source (entry 6), and the employment of NIS or molecular I_2 failed to give **6a** (entries 7 and 8).

With the optimized reaction conditions in hand, we then set out to explore the generality of the three-component reaction. We first applied the optimized conditions (Table 1, entry 10) to the synthesis of *ortho*-chloroarylphosphonates via the coupling of a variety of aryne precursors **1**, trialkyl phosphites **2**, and CCl_4, and the results were illustrated in Table 3. Pleasingly, the reactions of benzyne (generated from **1a**) with various trialkyl phosphites **2** and CCl_4 led to the formation of *ortho*-chloroarylphosphonates **4a−4e** in 42−80% isolated yields. We also tried the reactions with the use of other P(III) nucleophiles such as dimethyl phenylphosphonite **2f** and ethyl diphenylphosphinite **2g**, while both reactions failed to give the desired **4f** and **4g**. In addition, **2f** and **2g** were oxidized to give dimethyl phenylphosphonate and ethyl diphenylphosphinate, respectively. The employment of other symmetric arynes (generated from **1b** and **1c**) afforded **4h** and **4i** in good yields. We then turned to unsymmetric arynes, and 3-methoxy-substituted aryne (generated from **1d**) reacted cleanly with triethyl phosphite and CCl_4 to generate **4j** as a single isomer, which was in good agreement with the regioselectivity reported in the literature.[18] The employment of unsymmetric 4-substituted arynes (generated from **1e−1g**) bearing different groups (Me, OMe and OCF_3) produced **4k**/**4k′**−**4m**/**4m′** in 55−63% yields with two regioisomers, which further suggested

https://doi.org/10.1021/acs.joc.1c00550
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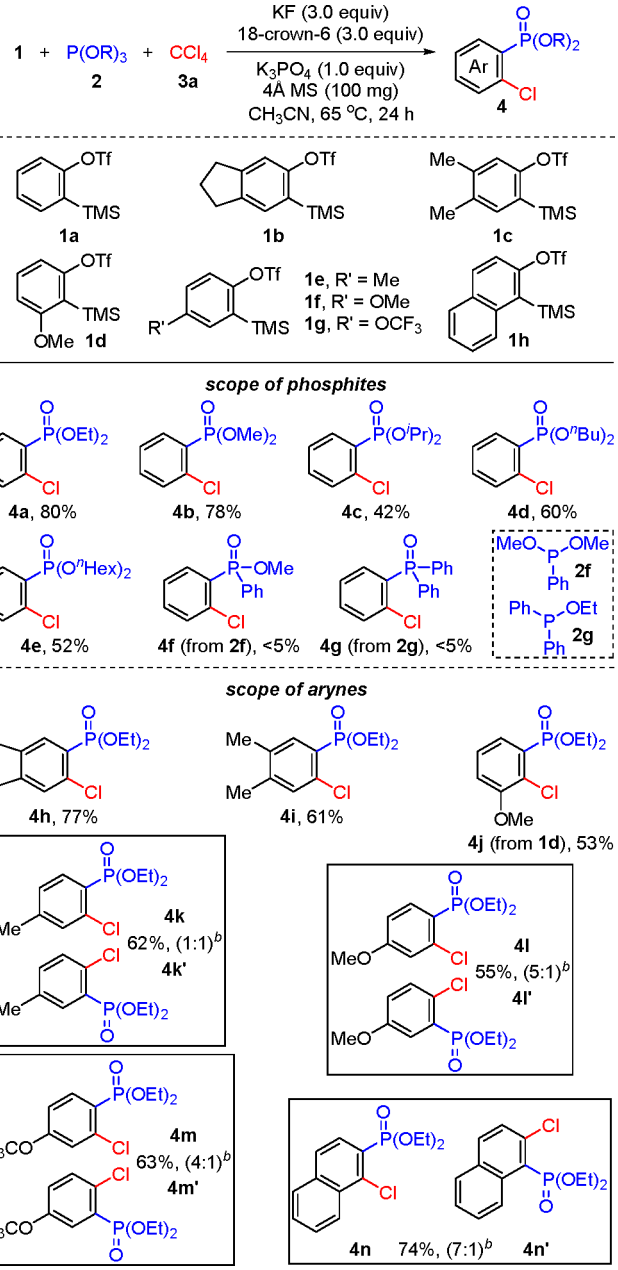
Table 3. Synthesis of *ortho*-Chloroarylphosphonates[a]

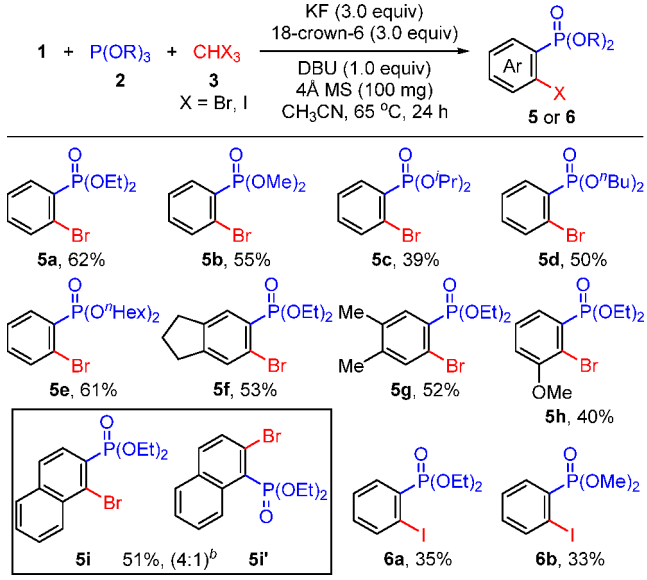


[a]Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), **3a** (3 mmol), KF (0.6 mmol), 18-crown-6 (0.6 mmol), K_3PO_4 (0.2 mmol), 4 Å MS (100 mg), CH_3CN (2 mL), 65 °C, 24 h. Isolated yield based on **2**. [b]The yield includes both major isomer **4** and minor isomer **4′**. The ratio was determined by $^{31}P\{^1H\}$ NMR.

that an aryne intermediate was involved in the reaction. Noteworthily, bulky 1,2-didehydronaphthalene (generated from **1h**) was also applicable to the reaction, leading to the formation of the desired **4n**/**4n′** (7:1) in 74% yield.

Next, the synthesis of *ortho*-bromoarylphosphonates and *ortho*-iodoarylphosphonates was carried out under the optimized conditions (Table 2, entry 5 or 6), and the results were illustrated in Table 4. The coupling of symmetric arynes, various trialkyl phosphites, and $CHBr_3$ provided *ortho*-bromoarylphosphonates **5a**−**5g** in 55−63% isolated yields. The desired **5h** was also obtained in 40% yield as a single isomer when the unsymmetric aryne precursor **1d** was

Table 4. Synthesis of *ortho*-Bromoarylphosphonates and *ortho*-Iodophenylphosphonates[a]

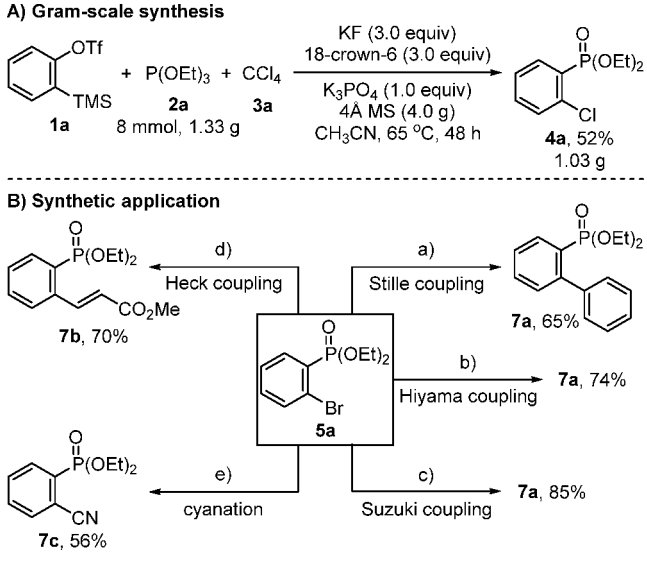


[a]Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), **3** (3 mmol of $CHBr_3$ or 0.6 mmol of CHI_3), KF (0.6 mmol), 18-crown-6 (0.6 mmol), DBU (0.2 mmol), 4 Å MS (100 mg), CH_3CN (2 mL), 65 °C, 24 h. Isolated yield based on **2**. [b]The yield includes both major isomer **5i** and minor isomer **5i′**. The ratio was determined by $^{31}P\{^1H\}$ NMR.

employed. In addition, silylaryl triflate **1h** underwent this reaction efficiently, delivering **5i**/**5i′** (4:1) in 51% yield. Moreover, the reaction of benzyne, triethyl or trimethyl phosphite, and CHI_3 afforded *ortho*-iodophenylphosphonates **6a** and **6b** in 35% and 33% yields, respectively.

To show the synthetic utility of our method, a scale-up experiment and transformation of the resultant product were conducted (Scheme 2). A gram-scale reaction of **2a** (1.33 g, 8.0 mmol) with **1a** (16 mmol) and CCl_4 (120 mmol) was conducted under the standard conditions, and the desired **4a** was isolated in 52% yield (1.03 g). The reaction of *ortho*-bromophenylphosphonate **5a** with $PhSnBu_3$ resulted in the

Scheme 2. Gram-Scale Synthesis and Synthetic Application

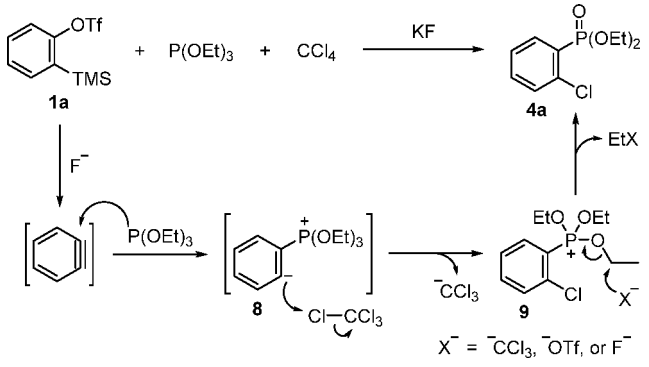


https://doi.org/10.1021/acs.joc.1c00550
J. Org. Chem. 2021, 86, 7010−7018

Stille coupling, leading to the formation of biarylphosphonate **7a** in 65% yield. Furthermore, both the Hiyama coupling of **5a** with $PhSi(OEt)_3$ and the Suzuki coupling of **5a** with $PhB(OH)_2$ smoothly afforded **7a** in good yields. We then turned to the Heck coupling, and the reaction of **5a** with methyl acrylate led to the desired **7b** in 70% yield. In addition, the cyanation of **5a** with CuCN gave *ortho*-cyanophenylphosphonate **7c** in 56% yield.

Based on the above experimental results and previous reports,[12,13,17] a plausible main reaction pathway for the formation of **4a** is outlined in Scheme 3. Benzyne, which is

Scheme 3. Proposed Mechanism



generated by fluoride-induced elimination of benzyne precursor **1a**, suffers a nucleophilic attack of triethyl phosphite to produce the 1,3-zwitterionic intermediate **8**, which is trapped by CCl_4 to form the intermediate **9**. The product **4a** is then obtained via subsequent Michaelis−Arbuzov type of mechanism[19] involving the participation of a fluoride ion or others. In addition, the formation of **5** and **6** could possibly be explained by the similar pathway of the formation of **4a**.

In conclusion, we have developed a novel three-component reaction of arynes with the use of a trialkyl phosphite as the nucleophile and a halide as the electrophile to prepare *ortho*-halogenated arylphosphonates in moderate to good yields under mild reaction conditions. The resultant products could be further used in organic synthesis and transformed into other *ortho*-functionalized arylphosphorus compounds. The good functional group compatibility and mild reaction conditions showcase the potential of this approach in chemical synthesis.

EXPERIMENTAL SECTION

General Details. Unless otherwise stated, commercially available reagents including dry solvents were used without additional purification. Acetonitrile was distilled from calcium hydride. THF was distilled from sodium. Petroleum ether refers to the petroleum fraction bp 40−90 °C. Commercial reagents were used without purification unless otherwise noted. Kobayashi's aryne precursors **1** which were not commercially available were prepared according to the literature.[16] Flash chromatography was performed using the indicated solvent system on silica gel standard grade (200−300 mesh). ^1H NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (400 MHz) spectrometer. $^{13}C\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (100 MHz) spectrometer. $^{31}P\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (162 MHz) spectrometer. $^{19}F\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker 400 (376 MHz) spectrometer. Chemical shifts are reported relative to $CDCl_3$ (δ 7.26 ppm) for ^1H NMR and $CDCl_3$ (δ 77.0 ppm) for $^{13}C\{^1H\}$ NMR. High-resolution mass spectra (HRMS) were recorded on a Q-Exactive Orbitrap mass spectrometer (Thermo, CA). Abbreviations for signal coupling are as follows: s = singlet, d = doublet; t = triplet, dd = doublet of doublets, m = multiplet, dt = double of triplets. The known compounds **4a**,[20] **4b**,[21] **4c**,[22] **4d**,[23] **5a**,[24] **5b**,[4e] **5c**,[25] **5i**,[26] **6a**,[27] **7a**,[28] **7b**,[29] and **7c**[30] showed characterization data in full agreement with previously reported data.

General Procedure for the Synthesis of Compounds 4. To a solution of 2-(trimethylsilyl)-phenyl triflate **1a** (119 mg, 0.4 mmol), triethyl phosphite **2a** (33 mg, 0.2 mmol), and CCl_4 **3a** (462 mg, 3.0 mmol) in acetonitrile (2 mL) were added K_3PO_4 (42 mg, 0.2 mmol), KF (35 mg, 0.6 mmol), 18-crown-6 (159 mg, 0.6 mmol), and 4 Å molecular sieves (100 mg). The mixture was stirred in an oil bath at 65 °C for 24 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **4a** (40 mg, 80%) as a yellow oil.

General Procedure for the Synthesis of Compounds 5. To a solution of 2-(trimethylsilyl)-phenyl triflate **1a** (119 mg, 0.4 mmol), triethyl phosphite **2a** (33 mg, 0.2 mmol), and $CHBr_3$ **3b** (756 mg, 3.0 mmol) in acetonitrile (2 mL) were added DBU (31 mg, 0.2 mmol), KF (35 mg, 0.6 mmol), 18-crown-6 (159 mg, 0.6 mmol), and 4 Å molecular sieves (100 mg). The mixture was stirred in an oil bath at 65 °C for 24 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **5a** (36 mg, 62%) as a yellow oil.

General Procedure for the Synthesis of Compounds 6. To a solution of 2-(trimethylsilyl)-phenyl triflate **1a** (119 mg, 0.4 mmol), triethyl phosphite **2a** (33 mg, 0.2 mmol), and CHI_3 **3c** (236 mg, 0.6 mmol) in acetonitrile (2 mL) were added DBU (31 mg, 0.2 mmol), KF (35 mg, 0.6 mmol), 18-crown-6 (159 mg, 0.6 mmol), and 4 Å molecular sieves (100 mg). The mixture was stirred in an oil bath at 65 °C for 24 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **6a** (24 mg, 35%) as a yellow oil.

Gram-Scale Synthesis. To a solution of 2-(trimethylsilyl)-phenyl triflate **1a** (4.77 g, 16 mmol), triethyl phosphite **2a** (1.33 g, 8.0 mmol), and CCl_4 **3a** (18.46 g, 120 mmol) in acetonitrile (80 mL) were added K_3PO_4 (1.70 g, 8.0 mmol), KF (1.39 g, 24 mmol), 18-crown-6 (6.34 g, 24 mmol), and 4 Å molecular sieves (4.0 g). The mixture was stirred in an oil bath at 65 °C for 48 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **4a** (1.03 g, 52%) as a yellow oil.

Synthetic Application (The Stille Coupling). A mixture of diethyl (2-bromophenyl)phosphonate **5a** (59 mg, 0.2 mmol), tributylphenyltin (88 mg, 0.24 mmol), $Pd(OAc)_2$ (1.4 mg, 0.006 mmol), DABCO (1.4 mg, 0.012 mmol), and TBAF (157 mg, 0.6 mmol) in 1,4-dioxane (2 mL) was taken under argon atmosphere in a sealed tube vial. The mixture was stirred in an oil bath at 100 °C for 24 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **7a** (38 mg, 65%) as a yellow oil.

Synthetic Application (The Hiyama Coupling). A mixture of diethyl (2-bromophenyl)phosphonate **5a** (59 mg, 0.2 mmol), phenyltriethoxysilane (96 mg, 0.4 mmol), $Pd(OAc)_2$ (1.4 mg, 0.006 mmol), DABCO (1.4 mg, 0.012 mmol), and TBAF (104 mg, 0.4 mmol) in 1,4-dioxane (2 mL) was taken under argon atmosphere in a sealed tube vial. The mixture was stirred in an oil bath at 80 °C for 24 h. After removal of the solvent, the residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **7a** (43 mg, 74%) as a yellow oil.

Synthetic Application (The Suzuki Coupling). A mixture of diethyl (2-bromophenyl)phosphonate **5a** (59 mg, 0.2 mmol), phenylboronic acid (36 mg, 0.3 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), and Na_2CO_3 (42 mg, 0.4 mmol) in toluene/water/ethanol (5/5/1, 2 mL) was taken under argon atmosphere in a sealed tube vial. The mixture was stirred in an oil bath at 100 °C for 24 h. The reaction mixture was then extracted with ethyl acetate (10 mL) for three times, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by flash column

https://doi.org/10.1021/acs.joc.1c00550
J. Org. Chem. 2021, 86, 7010−7018

chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **7a** (49 mg, 85%) as a yellow oil.

Synthetic Application (The Heck Coupling). A mixture of diethyl (2-bromophenyl)phosphonate **5a** (59 mg, 0.2 mmol), methyl acrylate (35 mg, 0.4 mmol), $Pd(PPh_3)_4$ (23 mg, 0.02 mmol), and Na_2CO_3 (42 mg, 0.4 mmol) in DMA (2 mL) was taken under argon atmosphere in a sealed tube vial. The mixture was stirred in an oil bath at 100 °C for 24 h. After the addition of water (5 mL) to the reactant, the mixture was then extracted with ethyl acetate (10 mL) five times, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **7b** (42 mg, 70%) as a yellow oil.

Synthetic Application (Cyanation). To a solution of diethyl (2-bromophenyl)phosphonate **5a** (59 mg, 0.2 mmol) in DMF (2 mL) was added CuCN (28 mg, 0.3 mmol). The mixture was stirred in an oil bath at reflux for 16 h. After the addition of water (5 mL) to the reactant, the mixture was then extracted with ethyl acetate (10 mL) five times, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was then purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (4:1) to give the pure product **7c** (27 mg, 56%) as a yellow oil.

*Diethyl (2-Chlorophenyl)phosphonate (**4a**).*[20] Yellow oil (40 mg, 80%); R_f = 0.24 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.97 (m, 1H), 7.47−7.44 (m, 2H), 7.38−7.32 (m, 1H), 4.25−4.08 (m, 4H), 1.35 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.8 (d, J = 3.0 Hz), 135.9 (d, J = 7.8 Hz), 133.5 (d, J = 2.6 Hz), 130.7 (d, J = 10.3 Hz), 127.4 (d, J = 190 Hz), 126.4 (d, J = 13.7 Hz), 62.5 (d, J = 5.5 Hz), 16.3 (d, J = 6.5 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 14.5.

*Dimethyl (2-Chlorophenyl)phosphonate (**4b**).*[21] Yellow oil (34 mg, 78%); R_f = 0.22 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01−7.94 (m, 1H), 7.49−7.45 (m, 2H), 7.38−7.32 (m, 1H), 3.81 (d, J = 11.4 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.8 (d, J = 3.0 Hz), 137.0 (d, J = 7.8 Hz), 133.8 (d, J = 2.6 Hz), 130.8 (d, J = 10.4 Hz), 126.4 (d, J = 13.8 Hz), 126.3 (d, J = 192 Hz), 52.9 (d, J = 5.7 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 17.6.

*Diisopropyl (2-Chlorophenyl)phosphonate (**4c**).*[22] Yellow oil (23 mg, 42%); R_f = 0.30 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−7.98 (m, 1H), 7.43−7.40 (m, 2H), 7.34−7.28 (m, 1H), 4.76−4.64 (m, 2H), 1.37 (d, J = 6.2 Hz, 6H), 1.24 (d, J = 6.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.7 (d, J = 2.7 Hz), 135.9 (d, J = 8.0 Hz), 133.2 (d, J = 2.7 Hz), 130.6 (d, J = 10.2 Hz), 128.7 (d, J = 190 Hz), 126.2 (d, J = 13.8 Hz), 71.3 (d, J = 5.7 Hz), 24.0 (d, J = 4.3 Hz), 23.6 (d, J = 4.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 12.0.

*Dibutyl (2-Chlorophenyl)phosphonate (**4d**).*[23] Yellow oil (37 mg, 60%); R_f = 0.33 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.96 (m, 1H), 7.47−7.45 (m, 2H), 7.37−7.32 (m, 1H), 4.18−3.99 (m, 4H), 1.72−1.63 (m, 4H), 1.46−1.36 (m, 4H), 0.91 (t, J = 7.4 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.8 (d, J = 2.9 Hz), 136.0 (d, J = 7.9 Hz), 133.5 (d, J = 2.6 Hz), 130.7 (d, J = 10.3 Hz), 127.4 (d, J = 191 Hz), 126.3 (d, J = 13.7 Hz), 66.2 (d, J = 5.9 Hz), 32.4 (d, J = 6.6 Hz), 18.7, 13.6; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 14.8.

*Dihexyl (2-Chlorophenyl)phosphonate (**4e**).* Yellow oil (38 mg, 52%); R_f = 0.35 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03−7.96 (m, 1H), 7.47−7.43 (m, 2H), 7.36−7.31 (m, 1H), 4.16−3.99 (m, 4H), 1.68 (dt, J = 14.6, 6.7 Hz, 4H), 1.40−1.33 (m, 4H), 1.29−1.25 (m, 8H), 0.86 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.8 (d, J = 3.0 Hz), 135.9 (d, J = 7.9 Hz), 133.5 (d, J = 2.6 Hz), 130.7 (d, J = 10.3 Hz), 127.5 (d, J = 191 Hz), 126.3 (d, J = 13.7 Hz), 66.5 (d, J = 5.9 Hz), 31.3, 30.4 (d, J = 6.6 Hz), 25.2, 22.5, 14.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 14.7; HRMS (ESI-Orbitrap) m/z: [M + H]$^+$ calcd for $C_{18}H_{31}{}^{35}ClO_3P$ 361.1694, found 361.1692.

*Diethyl (6-Chloro-2,3-dihydro-1H-inden-5-yl)phosphonate (**4h**).* Yellow oil (45 mg, 77%); R_f = 0.24 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 14.0 Hz, 1H), 7.30 (d, J = 5.1 Hz, 1H), 4.23−4.05 (m, 4H), 2.95−2.88 (m, 4H), 2.15−2.08 (m, 2H), 1.35 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 151.1 (d, J = 2.9 Hz), 142.8 (d, J = 14.3 Hz), 134.4 (d, J = 3.6 Hz), 131.7 (d, J = 8.3 Hz), 126.7 (d, J = 11.6 Hz), 124.2 (d, J = 191 Hz), 62.3 (d, J = 5.4 Hz), 33.0, 32.1, 25.4, 16.3 (d, J = 6.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 16.0; HRMS (ESI-Orbitrap) m/z: [M + H]$^+$ calcd for $C_{13}H_{19}{}^{35}ClO_3P$ 289.0755, found 289.0750.

*Diethyl (2-Chloro-4,5-dimethylphenyl)phosphonate (**4i**).* Yellow oil (34 mg, 61%); R_f = 0.25 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 14.3 Hz, 1H), 7.22 (d, J = 5.6 Hz, 1H), 4.22−4.03 (m, 4H), 2.26 (s, 3H), 2.27 (s, 3H), 1.33 (t, J = 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 143.3 (d, J = 2.8 Hz), 137.0 (d, J = 8.4 Hz), 135.2 (d, J = 13.9 Hz), 133.6 (d, J = 2.9 Hz), 131.6 (d, J = 11.0 Hz), 123.8 (d, J = 192 Hz), 62.3 (d, J = 5.4 Hz), 19.7, 19.0, 16.3 (d, J = 6.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 15.6; HRMS (ESI-Orbitrap) m/z: [M + H]$^+$ calcd for $C_{12}H_{19}{}^{35}ClO_3P$ 277.0755, found 277.0751.

*Diethyl (2-Chloro-6-methoxyphenyl)phosphonate (**4j**).* Yellow oil (29 mg, 53%); R_f = 0.31 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.32 (m, 1H), 7.07−7.04 (m, 1H), 6.87−6.84 (m, 1H), 4.27−4.13 (m, 4H), 3.88 (d, J = 1.4 Hz, 3H), 1.36 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 3.0 Hz), 138.1 (d, J = 4.2 Hz), 137.4 (d, J = 9.2 Hz), 118.6 (d, J = 198 Hz), 116.6 (d, J = 11.2 Hz), 112.0 (d, J = 14.5 Hz), 62.3 (d, J = 5.3 Hz), 55.6, 16.3 (d, J = 6.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 13.0; HRMS (ESI-Orbitrap) m/z: [M + H]$^+$ calcd for $C_{11}H_{17}{}^{35}ClO_4P$ 279.0548, found 279.0544.

*Diethyl (2-Chloro-4-methylphenyl)phosphonate (**4k**).* Yellow oil (16 mg, 31%); R_f = 0.32 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, J = 14.0, 7.8 Hz, 1H), 7.23 (d, J = 5.2 Hz, 1H), 7.12−7.09 (m, 1H), 4.19−4.02 (m, 4H), 2.33 (s, 3H), 1.30 (t, J = 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.6 (d, J = 2.7 Hz), 136.5 (d, J = 3.4 Hz), 135.8 (d, J = 8.1 Hz), 131.2 (d, J = 10.7 Hz), 127.1 (d, J = 14.0 Hz), 124.0 (d, J = 193 Hz), 62.3 (d, J = 5.5 Hz), 21.1, 16.2 (d, J = 6.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 15.2; HRMS (ESI-Orbitrap) m/z: [M + H]$^+$ calcd for $C_{11}H_{17}{}^{35}ClO_3P$ 263.0598, found 263.0596.

*Diethyl (2-Chloro-5-methylphenyl)phosphonate (**4k′**).* Yellow oil (16 mg, 31%); R_f = 0.35 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, J = 14.6, 2.1 Hz, 1H), 7.32 (dd, J = 8.2, 5.6 Hz, 1H), 7.26−7.25 (m, 1H), 4.24−4.05 (m, 4H), 2.35 (s, 3H), 1.34 (t, J = 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 136.6 (d, J = 8.3 Hz), 136.4, 134.3 (d, J = 2.7 Hz), 133.6 (d, J = 2.9 Hz), 130.5 (d, J = 10.8 Hz), 126.7 (d, J = 189 Hz), 62.4 (d, J = 5.5 Hz), 20.7, 16.3 (d, J = 6.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 15.0; HRMS (ESI-Orbitrap) m/z: [M + H]$^+$ calcd for $C_{11}H_{17}{}^{35}ClO_3P$ 263.0598, found 263.0596.

*Diethyl (2-Chloro-4-methoxyphenyl)phosphonate (**4l**).* Yellow oil (26 mg, 46%); R_f = 0.33 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 13.7, 8.6 Hz, 1H), 6.98 (dd, J = 4.6, 2.4 Hz, 1H), 6.85 (dt, J = 8.6, 2.5 Hz, 1H), 4.20−4.05 (m, 4H), 3.84 (s, 3H), 1.33 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 3.0 Hz), 138.1 (d, J = 4.2 Hz), 137.4 (d, J = 9.2 Hz), 118.6 (d, J = 198 Hz), 116.6 (d, J = 11.2 Hz), 112.0 (d, J = 14.6 Hz), 62.3 (d, J = 5.3 Hz), 55.6, 16.3 (d, J = 6.6 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 15.5; HRMS (ESI-Orbitrap) m/z: [M + H]$^+$ calcd for $C_{11}H_{17}{}^{35}ClO_4P$ 279.0548, found 279.0544.

*Diethyl (2-Chloro-4-(trifluoromethoxy)phenyl)phosphonate (**4m**).* Yellow oil (34 mg, 50%); R_f = 0.21 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (dd, J = 13.9, 8.5 Hz, 1H), 7.33−7.31 (m, 1H), 7.21−7.18 (m, 1H), 4.26−4.08 (m, 4H), 1.35 (t, J = 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 152.3 (d, J = 1.9 Hz), 138.3 (d, J = 3.9 Hz), 137.4 (d, J = 9.0 Hz), 126.2 (d, J = 194 Hz), 122.7 (d, J = 11.0 Hz), 120.2 (q, J_{C-F} = 260 Hz), 118.1 (d, J = 15.2 Hz), 62.8 (d, J = 5.6 Hz), 16.2 (d, J = 6.4 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 13.0; ^{19}F{^{1}H} NMR

https://doi.org/10.1021/acs.joc.1c00550
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(376 MHz, $CDCl_3$) δ −57.7; HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}{}^{35}ClF_3O_4P$ 333.0265, found 333.0262.

*Diethyl (1-Chloronaphthalen-2-yl)phosphonate (**4n**).* Yellow oil (39 mg, 65%); R_f = 0.25 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.47−8.43 (m, 1H), 8.03 (dd, J = 12.3, 8.5 Hz, 1H), 7.89−7.82 (m, 2H), 7.68−7.62 (m, 2H), 4.28−4.14 (m, 4H), 1.37 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.6 (d, J = 2.6 Hz), 136.1 (d, J = 2.3 Hz), 131.1 (d, J = 11.7 Hz), 129.7 (d, J = 7.8 Hz), 128.7, 128.2, 127.8 (d, J = 1.2 Hz), 126.8 (d, J = 13.6 Hz), 125.4 (d, J = 1.0 Hz), 124.7 (d, J = 190 Hz), 62.6 (d, J = 5.5 Hz), 16.3 (d, J = 6.6 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 15.1; HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{14}H_{17}{}^{35}ClO_3P$ 299.0598, found 299.0594.

*Diethyl (2-Bromophenyl)phosphonate (**5a**).*[24] Yellow oil (49 mg, 62%); R_f = 0.23 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01−7.95 (m, 1H), 7.65−7.61 (m, 1H), 7.39−7.32 (m, 2H), 4.22−4.05 (m, 4H), 1.32 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.2 (d, J = 8.3 Hz), 134.2 (d, J = 11.1 Hz), 133.5 (d, J = 2.7 Hz), 129.4 (d, J = 192 Hz), 126.8 (d, J = 13.6 Hz), 125.1 (d, J = 4.0 Hz), 62.5 (d, J = 5.6 Hz), 16.2 (d, J = 6.6 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 14.8.

*Dimethyl (2-Bromophenyl)phosphonate (**5b**).*[4e] Yellow oil (29 mg, 55%); R_f = 0.20 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02−7.96 (m, 1H), 7.71−7.65 (m, 1H), 7.43−7.37 (m, 2H), 3.82 (d, J = 11.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.4 (d, J = 8.3 Hz), 134.4 (d, J = 11.3 Hz), 133.8 (d, J = 2.8 Hz), 128.4 (d, J = 194 Hz), 127.0 (d, J = 13.8 Hz), 125.2 (d, J = 4.0 Hz), 53.0 (d, J = 5.6 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 17.8.

*Diisopropyl (2-Bromophenyl)phosphonate (**5c**).*[25] Yellow oil (25 mg, 39%); R_f = 0.28 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05−8.00 (m, 1H), 7.62−7.59 (m, 1H), 7.37−7.28 (m, 2H), 4.73−4.65 (m, 2H), 1.36 (d, J = 6.2 Hz, 6H), 1.23 (d, J = 6.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.2 (d, J = 8.4 Hz), 134.2 (d, J = 11.1 Hz), 133.2 (d, J = 2.8 Hz), 130.7 (d, J = 192 Hz), 126.7 (d, J = 13.6 Hz), 125.2 (d, J = 3.7 Hz), 71.4 (d, J = 5.7 Hz), 24.0 (d, J = 4.3 Hz), 23.6 (d, J = 4.8 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 12.2.

*Dibutyl (2-Bromophenyl)phosphonate (**5d**).* Yellow oil (35 mg, 50%); R_f = 0.33 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05−7.97 (m, 1H), 7.68−7.64 (m, 1H), 7.42−7.33 (m, 2H), 4.16−4.00 (m, 4H), 1.71−1.64 (m, 4H), 1.46−1.37 (m, 4H), 0.90 (t, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.3 (d, J = 8.3 Hz), 134.3 (d, J = 11.1 Hz), 133.5 (d, J = 2.7 Hz), 129.5 (d, J = 193 Hz), 126.9 (d, J = 13.5 Hz), 125.2 (d, J = 4.1 Hz), 66.2 (d, J = 5.9 Hz), 32.4 (d, J = 6.8 Hz), 18.7, 13.6; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 15.0; HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{14}H_{23}{}^{79}BrO_3P$ 349.0563, found 349.0557.

*Dihexyl (2-Bromophenyl)phosphonate (**5e**).* Yellow oil (49 mg, 61%); R_f = 0.35 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04−7.98 (m, 1H), 7.68−7.64 (m, 1H), 7.42−7.34 (m, 2H), 4.15−4.00 (m, 4H), 1.69 (dt, J = 14.6, 6.7 Hz, 4H), 1.41−1.34 (m, 4H), 1.29−1.25 (m, 8H), 0.86 (t, J = 6.9 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.3 (d, J = 8.1 Hz), 134.3 (d, J = 11.2 Hz), 133.5 (d, J = 2.7 Hz), 129.5 (d, J = 192 Hz), 126.8 (d, J = 13.6 Hz), 125.2 (d, J = 3.8 Hz), 66.6 (d, J = 5.8 Hz), 31.3, 30.4 (d, J = 6.6 Hz), 25.2, 22.5, 14.0; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 15.0; HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{18}H_{31}{}^{79}BrO_3P$ 405.1189, found 405.1184.

*Diethyl (6-Bromo-2,3-dihydro-1H-inden-5-yl)phosphonate (**5f**).* Yellow oil (35 mg, 53%); R_f = 0.22 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 13.9 Hz, 1H), 7.51 (d, J = 4.7 Hz, 1H), 4.20−4.06 (m, 4H), 2.92 (t, J = 8.4 Hz, 2H), 2.88 (t, J = 7.7 Hz, 2H), 2.14−2.06 (m, 2H), 1.35 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 151.3 (d, J = 2.9 Hz), 143.4 (d, J = 14.3 Hz), 132.2 (d, J = 8.7 Hz), 130.3 (d, J = 12.5 Hz), 126.2 (d, J = 192 Hz), 122.5 (d, J = 4.8 Hz), 62.4 (d, J = 5.4 Hz), 32.8, 32.1, 25.3, 16.3 (d, J = 6.7 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 16.2; HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{13}H_{19}{}^{79}BrO_3P$ 333.0250, found 333.0247.

*Diethyl (2-Bromo-4,5-dimethylphenyl)phosphonate (**5g**).* Yellow oil (33 mg, 52%); R_f = 0.23 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 14.3 Hz, 1H), 7.44 (d, J = 5.3 Hz, 1H), 4.20−4.06 (m, 4H), 2.27 (s, 3H), 2.24 (s, 3H), 1.35 (t, J = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.3 (d, J = 2.9 Hz), 137.5 (d, J = 8.8 Hz), 135.7 (d, J = 14.1 Hz), 135.2 (d, J = 11.8 Hz), 125.9 (d, J = 193 Hz), 121.8 (d, J = 3.8 Hz), 62.3 (d, J = 5.4 Hz), 19.6, 19.0, 16.3 (d, J = 6.6 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 15.7; HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{12}H_{19}{}^{79}BrO_3P$ 321.0250, found 321.0247.

*Diethyl (2-Bromo-3-methoxyphenyl)phosphonate (**5h**).* Yellow oil (26 mg, 40%); R_f = 0.30 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66−7.60 (m, 1H), 7.39−7.34 (m, 1H), 7.07 (dd, J = 8.3, 1.4 Hz, 1H), 4.24−4.07 (m, 4H), 3.92 (s, 3H), 1.35 (t, J = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.5 (d, J = 15.9 Hz), 131.0 (d, J = 190 Hz), 128.1 (d, J = 3.6 Hz), 128.0 (d, J = 5.2 Hz), 115.7 (d, J = 3.0 Hz), 114.9 (d, J = 4.6 Hz), 62.6 (d, J = 5.6 Hz), 56.6, 16.3 (d, J = 6.7 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 14.8; HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_{11}H_{17}{}^{79}BrO_4P$ 323.0042, found 323.0039.

*Diethyl (1-Bromonaphthalen-2-yl)phosphonate (**5i**).*[26] Yellow oil (28 mg, 41%); R_f = 0.23 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.50−8.46 (m, 1H), 8.04 (dd, J = 12.2, 8.4 Hz, 1H), 7.91−7.84 (m, 2H), 7.67−7.61 (m, 2H), 4.28−4.14 (m, 4H), 1.38 (t, J = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 136.0 (d, J = 2.3 Hz), 132.6 (d, J = 12.8 Hz), 130.3 (d, J = 8.1 Hz), 128.7, 128.5, 128.2, 128.1 (d, J = 3.6 Hz), 128.1, 127.6 (d, J = 191 Hz), 127.5 (d, J = 13.5 Hz), 62.6 (d, J = 5.5 Hz), 16.3 (d, J = 6.7 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) 15.5.

*Diethyl (2-Iodophenyl)phosphonate (**6a**).*[27] Yellow oil (24 mg, 35%); R_f = 0.22 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04−7.97 (m, 2H), 7.47−7.41 (m, 1H), 7.19−7.15 (m, 1H), 4.23−4.09 (m, 4H), 1.37 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.6 (d, J = 12.9 Hz), 136.2 (d, J = 9.0 Hz), 133.3 (d, J = 3.1 Hz), 133.1 (d, J = 192 Hz), 127.5 (d, J = 13.9 Hz), 97.4 (d, J = 5.7 Hz), 62.6 (d, J = 5.6 Hz), 16.3 (d, J = 6.8 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 14.9.

*Dimethyl (2-Iodophenyl)phosphonate (**6b**).* Yellow oil (21 mg, 33%); R_f = 0.20 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.06−7.94 (m, 2H), 7.48−7.43 (m, 1H), 7.21−7.17 (m, 1H), 3.81 (d, J = 11.3 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 141.6 (d, J = 13.0 Hz), 136.3 (d, J = 9.0 Hz), 133.6 (d, J = 3.0 Hz), 132.1 (d, J = 194 Hz), 127.6 (d, J = 13.7 Hz), 97.2 (d, J = 6.0 Hz), 53.0 (d, J = 5.8 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 17.9; HRMS (ESI-Orbitrap) m/z: $[M + H]^+$ calcd for $C_8H_{11}IO_3P$ 312.9485, found 312.9482.

*Diethyl [1,1′-Biphenyl]-2-ylphosphonate (**7a**).*[28] Yellow oil (the Stille coupling: 38 mg, 65%; the Hiyama coupling: 43 mg, 74%; the Suzuki coupling: 49 mg, 85%); R_f = 0.25 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.08−8.00 (m, 1H), 7.58−7.52 (m, 1H), 7.47−7.30 (m, 7H), 3.98−3.77 (m, 4H), 1.12 (t, J = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 146.0 (d, J = 9.8 Hz), 141.3 (d, J = 4.2 Hz), 133.7 (d, J = 9.7 Hz), 131.8 (d, J = 2.9 Hz), 131.2 (d, J = 14.1 Hz), 129.2, 127.4, 127.3, 126.9 (d, J = 187 Hz), 126.7 (d, J = 14.6 Hz), 61.7 (d, J = 6.0 Hz), 16.0 (d, J = 6.8 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 18.1.

*Methyl (E)-3-(2-(Diethoxyphosphoryl)phenyl)acrylate (**7b**).*[29] Yellow oil (42 mg, 70%); R_f = 0.21 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 15.9 Hz, 1H), 8.06−8.00 (m, 1H), 7.70−7.66 (m, 1H), 7.58−7.54 (m, 1H), 7.48−7.43 (m, 1H), 6.37 (d, J = 15.9 Hz, 1H), 4.25−4.05 (m, 4H), 3.82 (s, 3H), 1.32 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8, 143.2 (d, J = 4.7 Hz), 137.7 (d, J = 8.8 Hz), 134.4 (d, J = 9.5 Hz), 132.7 (d, J = 2.8 Hz), 129.2 (d, J = 14.7 Hz), 128.0 (d, J = 184 Hz), 127.1 (d, J = 13.3 Hz), 120.7, 62.4 (d, J = 5.7 Hz), 51.8, 16.2 (d, J = 6.2 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 17.4.

https://doi.org/10.1021/acs.joc.1c00550
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*Diethyl (2-Cyanophenyl)phosphonate (**7c**).*[30] Yellow oil (27 mg, 56%); R_f = 0.20 (petroleum ether/ethyl acetate = 4/1 as the eluent); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17−8.08 (m, 1H), 7.83−7.80 (m, 1H), 7.73−7.62 (m, 2H), 4.34−4.15 (m, 4H), 1.39 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.6 (d, J = 3.2 Hz), 134.5 (d, J = 16.4 Hz), 132.4 (d, J = 2.7 Hz), 132.3 (d, J = 188 Hz), 132.2 (d, J = 14.1 Hz), 117.1 (d, J = 5.8 Hz), 114.6 (d, J = 4.9 Hz), 63.2 (d, J = 6.0 Hz), 16.2 (d, J = 6.3 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 12.6.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00550.

Copies of ^{1}H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra for compounds **4**, **5**, **6**, and **7** (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the 100 Young Talents Programme of Guangdong University of Technology (No. 220413506), the Science and Technology Planning Project of Guangdong Province (Nos. 2017A010103044 and 2019A050510042), and the National Undergraduate Training Program for Innovation and Entrepreneurship (No. D202011292349499886) for financial support.

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