JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

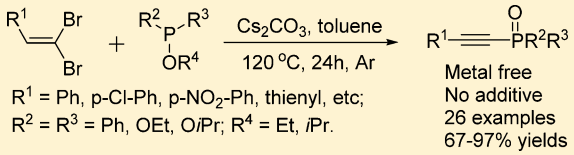
# $Cs_2CO_3$-Promoted One-Pot Synthesis of Alkynylphosphonates, -phosphinates, and -phosphine Oxides

Yulei Wang,[†] Jiepeng Gan,[†] Liu Liu,[†] Hang Yuan,[†] Yuxing Gao,*[,†] Yan Liu,*[,†] and Yufen Zhao[†,‡]

[†]Department of Chemistry, College of Chemistry and Chemical Engineering, and the Key Laboratory for Chemical Biology of Fujian Province and [‡]Department of Chemical Biology, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, China

Supporting Information

**ABSTRACT:** A novel and efficient $Cs_2CO_3$-promoted phosphorylation or phosphinylation of various 1,1-dibromo-1-alkenes with readily available trialkyl phosphites, ethyl diphenylphosphinite, or diethyl phenylphosphonite has been developed under metal-free conditions, providing a practical and powerful tool for one-pot synthesis of valuable alkynylphosphonates, -phosphinates, and -phosphine oxides in good to excellent yields.




Carbon−phosphorus bond construction for the synthesis of organophosphorus compounds is a fundamental and significant research topic in both organic synthesis and industrial processes during the past decades due to their increasing importance in organic synthesis, materials, and biology. Alkynyl-phosphorus compounds including alkynyl-phosphonates, -phosphinates, and -phosphine oxides are an important class of triple bond-containing, extremely versatile chemicals in modern organic chemistry, which are widely available for the preparation of structurally sophisticated phosphorus-containing compounds via reductions, hydrations, conjugate-addition reactions, metallacycle formation, and unique cycloaddition reactions.[1] Preparation of alkynylphosphorus compounds has aroused great interest among synthetic chemists for their important roles over the past decades, but the known highly efficient method is still rather limited. Apart from their traditional preparation from readily hydrolyzable $Ph_2P(O)Cl$ and Li or Mg acetylides,[1a] suffering from a lack of functionality tolerance, several methods for the synthesis of alkynylphosphonates or alkynylphosphine oxides have been developed recently including Pd-catalyzed cross-coupling from 1,1-dibromo-1-alkenes with H-phosphites,[2] Cu-catalyzed oxidative coupling of terminal alkynes with H-phosphonates,[3] Cu or Cu/Pd-bimetallic catalyzed decarboxylation,[4] and other approaches.[5] However, most of these methods suffer from poor substrate scopes, the need of extra additives or unsatisfactory yields, and in particular, the use of transition metals usually leads to the production of waste and has plenty of hazards associated with it.[6] Thus, there is still a strong need for developing more simple and efficient methods to prepare alkynyl-phosphorus compounds.

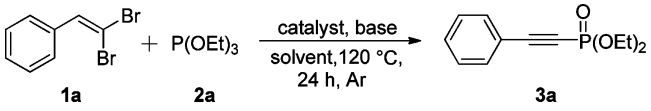
On the other hand, 1,1-dibromo-1-alkenes as terminal alkyne precursors are clearly emerging as fascinating and powerful building blocks for organic synthesis,[7] which can be conveniently prepared by the Corey−Fuchs reaction[8] and widely used in the transition-metal-catalyzed synthesis of disubstituted alkynes,[7a,9] ynamides,[7a,10] and ynol ethers[7a,11] owing to their ready availability and structural diversity. Enormous efforts have also been devoted to construct C−P bond following analogous protocols. Hayes and co-workers demonstrated the synthesis of alkynylphosphonates from 1,1-dibromoalkenes under the catalytic system of $Pd(OAc)_2$, dppf, or TFP, and propylene oxide in moderate yields early in 2000.[2] However, recent examples of Cu- or Ni-catalyzed reactions of vinyl dibromides with dialkyl phosphites or $HP(O)Ph_2$ only gave homologous vinyl phosphorus compounds[12] rather than alkynylphosphorus compounds since the Hirao reduction[13] was performed first. Even so, drawing from our experiences in the field of P−C bond construction,[14] we wondered whether the use of appropriate *P*-nucleophiles would avoid the Hirao reduction to realize a simple and general procedure for the synthesis of alkynylphosphorus compounds. To our delight, we found that three-coordinate trivalent phosphite esters such as triethyl phosphite could proceed well in this context. Herein, we describe a convenient and straightforward methodology for the preparation of alkynylphosphonates, -phosphinates, and -phosphine oxides through $Cs_2CO_3$-promoted and metal-free-catalyzed phosphorylation or phosphinylation of a wide range of 1,1-dibromo-1-alkenes.

To optimize the catalysis conditions, 1,1-dibromo-1-vinylbenzene **1a** and triethyl phosphite **2a** were chosed as the model substrates. Initially, when a mixture of **1a** (0.50 mmol), **2a** (0.55 mmol), $NiCl_2$ (0.05 mmol), Zn (1 mmol), 2,2′-bipyridine (bpy, 0.10 mmol), and $K_3PO_4$ (0.75 mmol) in toluene was heated at 120 °C for 24 h under dry argon, the desired product **3a** was formed in 28% $^{31}P$ NMR yield. This result indicated that our hypothesis was feasible, and hence, a deeper study of the reaction was conducted. We found that 37% yield of the desired product could be obtained under transition-metal-free conditions in the presence of $K_3PO_4$ (Table 1, entry 1).

**Received:** February 10, 2014
**Published:** March 24, 2014

   dx.doi.org/10.1021/jo500312n | J. Org. Chem. 2014, 79, 3678−3683

**Table 1. Optimization of Reaction Conditions**[a]




1a 2a 3a

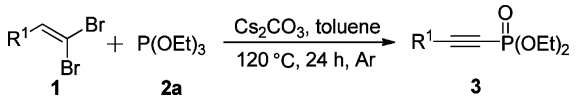
| entry | base | catalyst | solvent | yield[b] (%) |
|---|---|---|---|---|
| 1 | $K_3PO_4$ | | toluene | 37 |
| 2 | KOH | | toluene | 88 |
| 3 | KOH | | toluene | 87[c] |
| 4 | NaOH | | toluene | 45 |
| 5 | CsOH | | toluene | 88 |
| 6 | $K_2CO_3$ | | toluene | 7 |
| 7 | $Cs_2CO_3$ | | toluene | 91 (89) |
| 8 | NaOtBu | | toluene | 72 |
| 9 | KOtBu | | toluene | 66 |
| 10 | Et3N | | toluene | 0 |
| 11 | DBU | | toluene | 3 |
| 12 | $Cs_2CO_3$ | | 1,4-dioxane | 32 |
| 13 | $Cs_2CO_3$ | | DMF | 8 |
| 14 | $Cs_2CO_3$ | $NiBr_2$ | toluene | 26 |
| 15 | $Cs_2CO_3$ | $ZnBr_2$ | toluene | trace |
| 16 | $Cs_2CO_3$ | $PdCl_2$ | toluene | 40 |
| 17 | $Cs_2CO_3$ | | toluene | 85[d] |
| 18 | $Cs_2CO_3$ | | toluene | 11[e] |
| 19 | $Cs_2CO_3$ | | toluene | 49[f] |
| 20 | $Cs_2CO_3$ | | toluene | 60[g] |

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.55 mmol), base (0.75 mmol), catalyst (0.05 mmol), solvent (1.5 mL), 120 °C, 24 h, under Ar. [b]$^{31}$P NMR yields; yield after purification by silica gel chromatography in parenthese. [c]Denotes use of semiconductor-grade KOH. [d]12 h. [e]At 100 °C. [f]Using 0.5 mmol base. [g]Under dry Air.

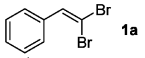
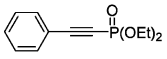
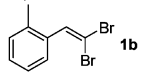
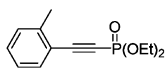
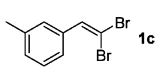
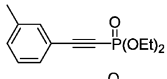
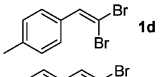
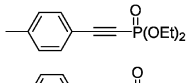
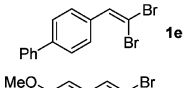
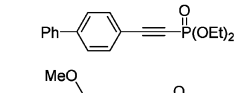
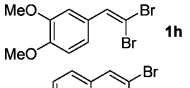
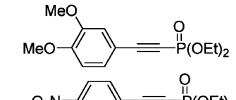
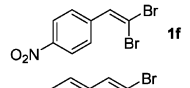
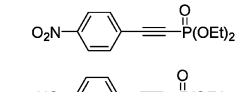
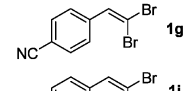
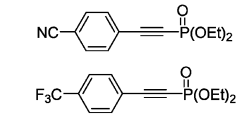
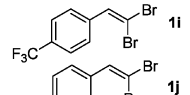
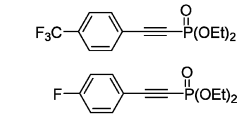
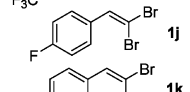
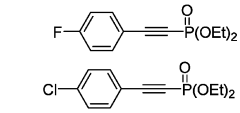
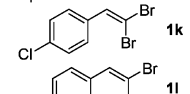
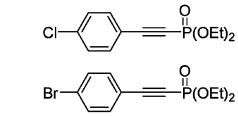
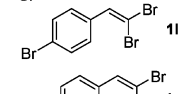
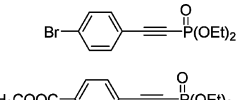
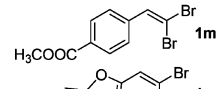
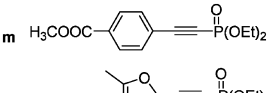
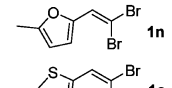
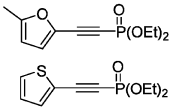
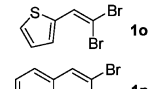
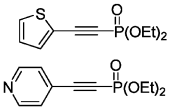
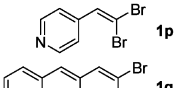
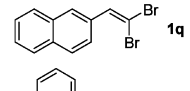
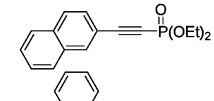
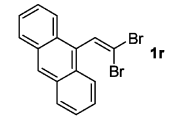
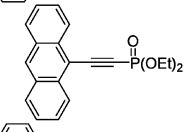
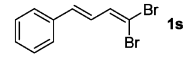
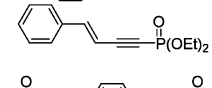
Obvious improvement in the yield of **3a** was achieved when stronger base KOH was used (entry 2). While some "transition-metal-free" reactions turned out to be catalyzed by a trace amount of Cu or Pd contamination,[15] semiconductor-grade KOH, 99.99% pure based on trace metal analysis, was also examined (entry 3). Subsequently, a screening of various bases such as NaOH, CsOH, $K_2CO_3$, $Cs_2CO_3$, *t*-BuOK, *t*-BuONa, $Et_3N$, and DBU illustrated that $Cs_2CO_3$ was the most effective base to generate the desired product **3a** in 91% yield (entries 4−11). The type of solvent was vital to the progress of the reaction. It was found that toluene was the best solvent, 1,4-dioxane afforded mild reaction yield, and DMF was a poor solvent (entries 7, 12, and 13). Although $NiBr_2$, $ZnBr_2$, and $PdCl_2$ were reported to be very effective in promoting the reaction of trialkyl phosphite and halohydrocarbon,[16] it was not available in the present reaction and gave poor yields (entries 14−16). Decreasing the reaction temperature to 100 °C led to a lower yield of 11% (entry 18). The loading of $Cs_2CO_3$ was also evaluated, and the use of 0.5 mmol of $Cs_2CO_3$ resulted in a significant decrease in yield (entry 19). The reaction afforded a lower yield of 60% under dry air (entry 20).

Under the optimal reaction conditions, we next explored the phosphorylation of various 1,1-dibromo-1-alkenes with triethyl phosphite to examine the generality of the methodology. As shown in Table 2, various valuable alkynylphosphonates can be conveniently and efficiently obtained by this novel $Cs_2CO_3$-promoted phosphorylation reaction of 1,1-dibromo-1-alkenes, and the corresponding products were produced in good to excellent yields (**3a−t**). In general, the transition-metal-free conditions are compatible with a range of functional groups.

**Table 2. $Cs_2CO_3$-Promoted Phosphorylation of *gem*-Dibromoalkenes with Triethyl Phosphite**[a]




1 2a 3

| Entry | 1 | 3 | Yield (%) |
|---|---|---|---|
| 1 |  1a |  3a | 89 |
| 2 |  1b |  3b | 81 |
| 3 |  1c |  3c | 80 |
| 4 |  1d |  3d | 84 |
| 5 |  1e |  3e | 91 |
| 6 |  1h |  3f | 87 |
| 7 |  1f |  3g | 91 |
| 8 |  1g |  3h | 97 |
| 9 |  1i |  3i | 78 |
| 10 |  1j |  3j | 86 |
| 11 |  1k |  3k | 84 |
| 12 |  1l |  3l | 82 |
| 13 |  1m |  3m | 89 |
| 14 |  1n |  3n | 72 |
| 15 |  1o |  3o | 96 |
| 16 |  1p |  3p | 76 |
| 17 |  1q |  3q | 83 |
| 18 |  1r |  3r | 88 |
| 19 |  1s |  3s | 82[b] |
| 20 |  1t |  3t | 90[c] |
| 21 |  1u |  3au | N.D.[d] |

[a]Reaction conditions: **1**(0.5 mmol), **2a** (0.55 mmol), $Cs_2CO_3$ (0.75 mmol), toluene (1.5 mL), 120 °C, 24 h, under Ar. [b]100 h. [c]Using **2a** 1.1 mmol and $Cs_2CO_3$ 1.5 mmol. [d]ND, not detected.

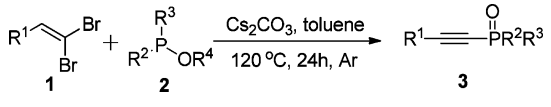
Thus, both electron-rich and electron-deficient 1,1-dibromo-1-alkenes were suitable for this method. A variety of functionalities, such as methyl (**3b−d**), phenyl (**3e**), alkoxyl

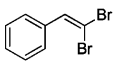
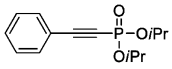
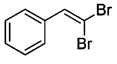
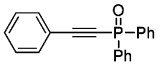
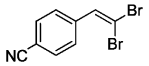
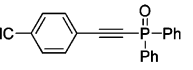
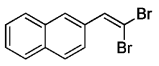
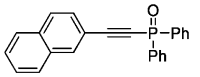
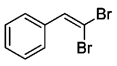
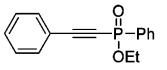
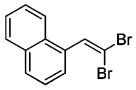
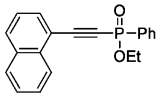

dx.doi.org/10.1021/jo500312n | J. Org. Chem. 2014, 79, 3678−3683

(**3f**), nitro (**3g**), cyano (**3h**), trifluoromethyl (**3i**), fluoro (**3j**), chloro (**3k**), bromo (**3l**), and carboxyl (**3m**) groups, were all tolerated. Generally, electron-poor substrates showed better reactivity and higher yields than electron-rich ones. Notably, heteroaromatic *gem*-dibromoalkenes such as **1n−p** could also be used as substrates to give high yields up to 96%. Interestingly, styryl *gem*-dibromoalkene (**1s**) having a reactive allene unit could also be used in the reaction to give the desired alkynylphosphonates selectively in 82% yield in spite of a longer reaction time of 100 h without damaging the other functionalities. More interestingly, as exemplified by entry 20, two phosphonate groups were easily introduced into bis-dibromide such as 1,4-bis(2,2-dibromovinyl)benzene **1t**, thus affording the corresponding product **3t** in 90% yield without the generation of monophosphorylation product. Unfortunately, the reaction did not occur using alkyl-substituted *gem*-dibromoalkenes as substrates such as octyl *gem*-dibromoalkene **1u**, probably since aromatic groups could stabilize the carbanion intermediate B (see Scheme 2) but alkyl groups destabilized it (entry 21).

To gain more insight into the substrate scope, various *P*-nucleophiles were investigated (Table 3). In addition to triethyl phosphite **2a**, triisopropyl phosphite **2b** could also be used in the reaction to give the desired product **4a** in 81% yield (entry 1). Gratifyingly, ethyl diphenylphosphinite **2c** also exhibited good compatibility. Thus, the corresponding alkynylphosphine oxides **3v**, **3w**, and **3x** were obtained in 67%, 75%, and 82% yields, respectively (entries 2−4). In addition, diethyl phenylphosphonite **2d** could also be transformed to the corresponding phosphinylated products in high yield (entries 5 and 6). Obviously, this protocol with broad substrate scope afforded a general and practical protocol for the preparation of various valuable alkynylphosphonates, -phosphinates, and -phosphine oxides.

**Table 3. $Cs_2CO_3$-Promoted Phosphorylation/ Phosphinylation of *gem*-Dibromoalkenes with P-Nucleophiles[a]**

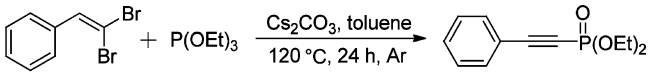



| Entry | 1 | 2 | 3 | Yield (%) |
|---|---|---|---|---|
| 1 |  1a | $P(OiPr)_3$ 2b |  3u | 81 |
| 2 |  1a | $Ph_2POEt$ 2c |  3v | 67 |
| 3 |  1g | $Ph_2POEt$ 2c |  3w | 75 |
| 4 |  1q | $Ph_2POEt$ 2c |  3x | 82 |
| 5 |  1a | $PhP(OEt)_2$ 2d |  3y | 80 |
| 6 |  1z | $PhP(OEt)_2$ 2d |  3z | 83 |

[a]Reaction conditions: **1** (0.5 mmol), **2** (0.55 mmol), $Cs_2CO_3$ (0.75 mmol), toluene(1.5 mL), 120 °C, 24 h, under Ar. [b]30 h.

It is worth noting that the reaction can also proceed well on gram scale with comparable yield (Scheme 1).

**Scheme 1. Reaction performed on grams scale**




15 mmol 16.5 mmol 3.21 g 85%

To understand the mechanism, several control reactions have been carried out (Scheme 2). Without bases, no desired product was observed. Examining the reaction of 1,1-dibromo-1-vinylbenzene **1a** with 1.5 equiv of $Cs_2CO_3$ at 120 °C in toluene for 24 h gave 1-(2-bromoethynyl)benzene in 91% yield. Subsequent treatment of 1-(2-bromoethynyl)benzene with 1.1 equiv of triethyl phosphite in toluene at 120 °C for 24 h under argon afforded the desired alkynylphosphonate **3a** in 99% $^{31}P$ NMR yield in the presence or absence of bases. Based on these results, it is reasonable that the reaction pathway first proceeded via the HBr elimination reaction to provide intermediate A.[17] Then A reacted with triethyl phosphate leading to the formation of quaternary phosphonium salt **C**. Finally, **C** underwent Michaelis−Arbuzov-type reaction to give the desired product **1c**.[1a,18]

In conclusion, we have successfully developed a simple and highly efficient approach to prepare a series of valuable alkynylphosphonates, -phosphinates, and -phosphine oxides starting from readily available 1,1-dibromo-1-alkenes. Importantly, this reaction is performed without the need of a transition-metal catalyst, a ligand, or an additive, and various valuable products can be conveniently obtained in a one-pot process. The remarkable functional group tolerance, operational simplicity of the procedure, and good to excellent yields mean that this reaction will find broad applications in various fields.

## EXPERIMENTAL SECTION

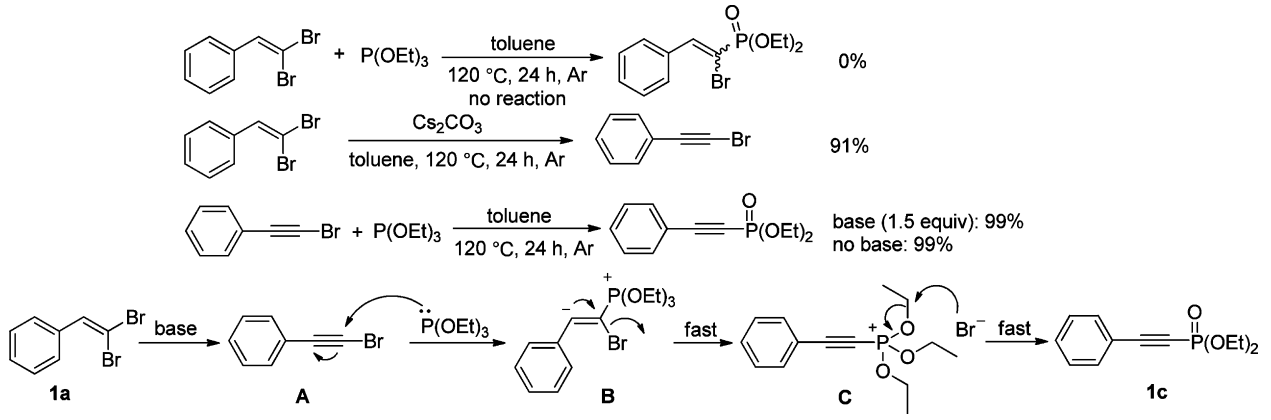
**General Information.** All reactions were carried out in Schlenk tubes under an argon atmosphere. Toluene was freshly distilled over sodium and benzophenone under Ar. Triethyl phosphite was purchased and further purified by extraction with petroleum ether and water system. The 1,1-dibromo-1-alkenes were prepared from the corresponding aldehydes. All the other reagents were purchased from commercial sources and used without further purification. Column chromatography was performed on silica gel 300−400 mesh. $^1H$, $^{13}C$, and $^{31}P$ NMR spectra were measured on a 400 MHz spectrometer with $CDCl_3$ as solvent using tetramethylsilane (TMS) as internal standard and 85% $H_3PO_4$ as external standard for $^{31}P$ NMR. HRMS spectra were recorded on a FT-MS apparatus. The CAS numbers of known compounds are listed.

**General Procedure for the Synthesis of 3a−z.** An oven-dried Schlenk tube with 0.75 mmol of $Cs_2CO_3$ was evacuated and purged with argon more than three times. A mixture of 1,1-dibromo-1-alkene (0.50 mmol) and *P*-nucleophiles (0.55 mmol) in toluene (1.5 mL) was added to the tube and stirred at 120 °C for 24 h. The suspension was filtered and washed with EtOAc (3 × 5 mL). The combined solvent was removed under reduced pressure. The residue was purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent.

*Diethyl (Phenylethynyl)phosphonate (**3a**) (CAS No. 3450-67-7).* 106 mg, 89% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.56−7.54 (m, 2H), 7.46−7.42 (m, 1H), 7.38−7.34 (m, 2H), 4.25−4.18 (m, 4H), 1.41−1.37 (t, $J$ = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 132.7 (d, $J_{C-P}$ = 2.5 Hz), 130.7, 128.6, 119.6 (d, $J_{C-P}$ = 5.6 Hz), 99.1 (d, $J_{C-P}$ = 52.7 Hz), 78.4 (d, $J_{C-P}$ = 300.3 Hz), 63.2 (d, $J_{C-P}$ = 5.4 Hz),


dx.doi.org/10.1021/jo500312n | J. Org. Chem. 2014, 79, 3678−3683

**Scheme 2. Mechanistic Studies**




16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −6.04. HRMS $m/z$ (ESI): calcd for $C_{12}H_{15}O_3P$ [M + Na]$^+$ 261.0657, found 261.0660.

*Diethyl (o-Tolylethynyl)phosphonate (**3b**) (CAS No. 139961-20-9).* 102 mg, 81% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.50−7.48 (d, $J$ = 7.6 Hz, 1H), 7.33−7.29 (t, $J$ = 7.9 Hz, 1H), 7.22−7.20 (d, $J$ = 7.6 Hz, 1H), 7.17−7.13 (t, $J$ = 7.7 Hz, 1H), 4.24−4.17(m, 4H), 2.44(s, 3H), 1.40−1.36 (t, $J$ = 6.9 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 141.8 (d, $J_{C-P}$ = 2.0 Hz), 133.0 (d, $J_{C-P}$ = 2.6 Hz), 130.7, 129.8, 125.8, 119.4 (d, $J_{C-P}$ = 5.3 Hz), 98.2 (d, $J_{C-P}$ = 52.6 Hz), 82.0 (d, $J_{C-P}$ = 299.7 Hz), 63.2 (d, $J_{C-P}$ = 5.2 Hz), 20.5, 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −5.85. HRMS $m/z$ (ESI): calcd for $C_{13}H_{17}O_3P$ [M + Na]$^+$ 275.0813, found 275.0814.

*Diethyl (m-Tolylethynyl)phosphonate (**3c**) (CAS No. 1315481-71-0).* 101 mg, 80% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.36−7.34 (m, 2H), 7.26−7.23 (m, 2H), 4.24−4.16(m, 4H), 2.32(s, 3H), 1.40−1.37 (t, $J$ = 7.1 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 138.4, 133.1 (d, $J_{C-P}$ = 2.5 Hz), 131.6, 129.7 (d, $J_{C-P}$ = 2.4 Hz), 128.5, 119.3 (d, $J_{C-P}$ = 5.7 Hz), 99.4 (d, $J_{C-P}$ = 53.5 Hz), 77.9 (d, $J_{C-P}$ = 300.6 Hz), 63.2 (d, $J_{C-P}$ = 5.4 Hz), 21.1, 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −5.90. HRMS $m/z$ (ESI): calcd for $C_{13}H_{17}O_3P$ [M + Na]$^+$ 275.0813, found 275.0810.

*Diethyl (p-Tolylethynyl)phosphonate (**3d**) (CAS No. 176100-−86-0).* 106 mg, 84% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.43−7.41 (d, $J$ = 8.0 Hz, 2H), 7.16−7.14 (d, $J$ = 8.0 Hz, 2H), 4.23−4.15 (m, 4H), 2.35(s, 3H), 1.39−1.35 (t, $J$ = 7.1 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 141.3, 132.6 (d, $J_{C-P}$ = 2.3 Hz), 129.6, 116.4 (d, $J_{C-P}$ = 5.6 Hz), 99.6 (d, $J_{C-P}$ = 53.3 Hz), 77.8 (d, $J_{C-P}$ = 300.6 Hz), 63.1 (d, $J_{C-P}$ = 5.4 Hz), 21.7, 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −5.68. HRMS $m/z$ (ESI): calcd for $C_{13}H_{17}O_3P$ [M + Na]$^+$ 275.0813, found 275.0809.

*Diethyl ((4-Phenylphenyl)ethynyl)phosphonate (**3e**) (CAS No. 912486-03-4).* 143 mg, 91% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.64−7.55 (m, 6H), 7.46−7.43 (m, 2H), 7.39−7.35 (m, 1H), 4.28−4.20 (m, 4H), 1.43−1.40 (t, $J$ = 7.1 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 143.5, 139.7, 133.1 (d, $J_{C-P}$ = 2.4 Hz), 129.0, 128.2, 127.2, 127.1, 118.3 (d, $J_{C-P}$ = 5.5 Hz), 99.1 (d, $J_{C-P}$ = 52.9 Hz), 79.0 (d, $J_{C-P}$ = 300.4 Hz), 63.2 (d, $J_{C-P}$ = 5.5 Hz), 16.1 (d, $J_{C-P}$ = 6.9 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −6.54. MS-ESI: $m/z$ 337.5 [M + Na]$^+$.

*Diethyl ((3,4-Dimethoxyphenyl)ethynyl)phosphonate (**3f**) (CAS No. 947504-11-2).* 129 mg, 87% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.16−7.14 (d, $J$ = 8.5 Hz, 1H), 6.99 (s, 1H), 6.80−6.78 (d, $J$ = 8.5 Hz, 1H), 4.22−4.14 (m, 4H), 3.86 (d, $J$ = 1.2 Hz, 3H), 3.83 (d, $J$ = 1.0 Hz, 3H), 1.38−1.34 (m, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 151.5, 148.8, 126.9 (d, $J_{C-P}$ = 2.6 Hz), 114.9 (d, $J_{C-P}$ = 2.1 Hz), 111.4 (d, $J_{C-P}$ = 5.8 Hz), 99.7 (d, $J_{C-P}$ = 53.9 Hz), 77.0(d, $J_{C-P}$ = 302.1 Hz), 63.1 (d, $J_{C-P}$ = 5.2 Hz), 56.0, 55.9, 16.1 (d, $J_{C-P}$ = 7.1 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −5.53. HRMS $m/z$ (ESI): calcd for $C_{14}H_{19}O_5P$ [M + Na]$^+$ 321.0868, found 321.0866.

*Diethyl ((4-Nitrophenyl)ethynyl)phosphonate (**3g**) (CAS No. 287960-25-2).* 128 mg, 91% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.24−8.22 (d, $J$ = 8.5 Hz, 2H), 7.73−7.7 (d, $J$ = 8.8 Hz, 2H), 4.27−4.20 (m, 4H), 1.42−1.38 (t, $J$ = 7.2 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$) $\delta$ 148.5, 133.5 (d, $J_{C-P}$ = 2.4 Hz), 126.1 (d, $J_{C-P}$ = 5.6 Hz), 123.7, 95.5 (d, $J_{C-P}$ = 51.7 Hz), 83.1 (d, $J_{C-P}$ = 293.0 Hz), 63.6 (d, $J_{C-P}$ = 5.6 Hz), 16.1 (d, $J_{C-P}$ = 6.8 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −7.45. HRMS $m/z$ (ESI): calcd for $C_{12}H_{14}NO_5P$ [M + Na]$^+$ 306.0507, found 306.0509.

*Diethyl ((4-Cyanophenyl)ethynyl)phosphonate (**3h**) (New Compound).* Oil; 128 mg, 97% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.67−7.62 (m, 4H), 4.24−4.17 (m, 4H), 1.40−1.36 (t, $J$ = 7.1 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 133.1 (d, $J_{C-P}$ = 2.4 Hz), 132.2, 124.3 (d, $J_{C-P}$ = 5.6 Hz), 117.7, 114.1, 96.9 (d, $J_{C-P}$ = 52.1 Hz), 82.5 (d, $J_{C-P}$ = 293.6 Hz), 63.5 (d, $J_{C-P}$ = 5.6 Hz), 16.1 (d, $J_{C-P}$ = 6.8 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −7.29. HRMS $m/z$ (ESI): calcd for $C_{13}H_{14}NO_3P$ [M + Na]$^+$ 286.0609, found 286.0603.

*Diethyl ((4-(Trifluoromethyl)phenyl)ethynyl)phosphonate (**3i**) (CAS No. 1315481-74-3).* 119 mg, 78% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.65−7.63 (d, $J$ = 8.3 Hz, 2H), 7.60−7.58 (d, $J$ = 8.4 Hz, 2H), 4.24−4.16 (m, 4H), 1.39−1.35 (t, $J$ = 7.2 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 132.9 (d, $J_{C-P}$ = 2.5 Hz), 132.2 (q, $J_{F-C}$ = 33.1 Hz), 125.5 (q, $J_{F-C}$ = 3.9 Hz), 123.4 (q, $J_{F-C}$ = 272.2 Hz), 123.3 (d, $J_{C-P}$ = 5.7 Hz), 96.6 (d, $J_{C-P}$ = 52.3 Hz), 80.7 (d, $J_{C-P}$ = 295.6 Hz), 63.4(d, $J_{C-P}$ = 5.6 Hz), 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −6.96. HRMS $m/z$ (ESI): calcd for $C_{13}H_{14}F_3O_3P$ [M + Na]$^+$ 329.0530, found 329.0527.

*Diethyl ((4-Fluorophenyl)ethynyl)phosphonate (**3j**) (CAS No. 176100-85-9).* 110 mg, 86% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.58−7.54 (dd, $J_{F-H}$ = 5.8 Hz, $J$ = 8.8 Hz, 2H), 7.09−7.05 (m, 2H), 4.24−4.16 (m, 4H), 1.42−1.38 (dt, $J_{H-P}$ = 0.5 Hz, 7.1 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 163.9 (d, $J_{F-C}$ = 255.9 Hz), 134.8 (dd, $J_{C-P}$ = 2.4 Hz, $J_{F-C}$ = 8.8 Hz), 129.0 (d, $J_{F-C}$ = 22.4 Hz), 115.7 (dd, $J_{F-C}$ = 3.6 Hz, $J_{C-P}$ = 5.7 Hz), 97.8 (d, $J_{C-P}$ = 53.0 Hz), 78.4 (d, $J_{C-P}$ = 300.5 Hz), 63.2(d, $J_{C-P}$ = 5.6 Hz), 16.1 (d, $J_{C-P}$ = 7.1 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −6.18. HRMS $m/z$ (ESI): calcd for $C_{12}H_{14}FO_3P$ [M + Na]$^+$ 279.0562, found 279.0559.

*Diethyl ((4-Chlorophenyl)ethynyl)phosphonate (**3k**) (CAS No. 176511-86-7).* 114 mg, 84% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.47−7.45 (d, $J$ = 8.6 Hz, 2H), 7.34−7.32 (d, $J$ = 8.6 Hz, 2H), 4.24−4.15 (m, 4H), 1.39−1.35 (dt, $J$ = 0.6 Hz, 7.1 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 137.1, 133.8 (d, $J_{C-P}$ = 2.5 Hz), 129.0, 118.0 (d, $J_{C-P}$ = 5.7 Hz), 97.6 (d, $J_{C-P}$ = 53.0 Hz), 79.6 (d, $J_{C-P}$ = 298.9 Hz), 63.3(d, $J_{C-P}$ = 5.3 Hz), 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): $\delta$ −6.42. HRMS $m/z$ (ESI): calcd for $C_{12}H_{14}ClO_3P$ [M + Na]$^+$ 295.0267, found 295.0266.

*Diethyl ((4-Bromophenyl)ethynyl)phosphonate (**3l**) (CAS No. 1345719-55-2).* 130 mg, 82% yield. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.50−7.48 (d, $J$ = 8.6 Hz, 2H), 7.40−7.38 (d, $J$ = 8.6 Hz, 2H), 4.23−4.15 (m, 4H), 1.39−1.36 (t, $J$ = 7.1 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 133.9 (d, $J_{C-P}$ = 2.3 Hz), 132.0, 125.4, 118.5 (d, $J_{C-P}$ = 5.7 Hz), 97.6 (d, $J_{C-P}$ = 52.7 Hz), 79.7 (d, $J_{C-P}$ = 297.1 Hz), 63.3 (d, $J_{C-P}$ = 5.5 Hz), 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$):


dx.doi.org/10.1021/jo500312n | J. Org. Chem. 2014, 79, 3678−3683

$\delta$ −5.90. HRMS $m/z$ (ESI): calcd for $C_{12}H_{14}BrO_3P$ $[M + Na]^+$ 338.9762, found 338.9762.

*Methyl ((4-Diethoxyphosphoryl)ethynyl)benzoate (**3m**) (New Compound).* Oil; 132 mg, 89% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.01−7.99 (d, $J$ = 8.5 Hz, 2H), 7.60−7.58 (d, $J$ = 8.0 Hz, 2H), 4.24−4.16 (m, 4H), 3.89 (s, 3H), 1.39−1.35 (t, $J$ = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 165.9, 132.5 (d, $J_{C-P}$ = 2.4 Hz), 131.8, 129.6, 123.9 (d, $J_{C-P}$ = 5.4 Hz), 97.4 (d, $J_{C-P}$ = 53.7 Hz), 81.0(d, $J_{C-P}$ = 295.1 Hz), 63.4(d, $J_{C-P}$ = 5.4 Hz), 52.4, 16.1 (d, $J_{C-P}$ = 6.9 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −6.79. HRMS $m/z$ (ESI): calcd for $C_{14}H_{17}O_5P$ $[M + Na]^+$ 319.0711, found 319.0709.

*Diethyl ((5-Methylfuran-2-yl)ethynyl)phosphonate (**3n**) (CAS No. 947504-11-2).* 87 mg, 72% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 6.76−6.75 (d, $J$ = 3.3 Hz, 1H), 6.01−6.00 (m, 1H), 4.21−4.13 (m, 4H), 2.29 (m, 3H), 1.37−1.33 (t, $J$ = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 156.4, 132.8 (d, $J_{C-P}$ = 6.7 Hz), 121.6, 107.7, 89.4 (d, $J_{C-P}$ = 53.8 Hz), 83.3 (d, $J_{C-P}$ = 296.4 Hz), 63.3 (d, $J_{C-P}$ = 5.6 Hz), 16.1 (d, $J_{C-P}$ = 7.0 Hz), 13.9. $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −6.25. HRMS $m/z$ (ESI): calcd for $C_{11}H_{15}O_4P$ $[M + Na]^+$ 265.0606, found 265.0604.

*Diethyl (Thiophene-2-ylethynyl)phosphonate (**3o**) (CAS No. 80034-76-0).* 117 mg, 96% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.42−7.40 (m, 2H), 7.01−6.99 (m, 1H), 4.22−4.15 (m, 4H), 1.38−1.35 (t, $J$ = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 135.9 (d, $J_{C-P}$ = 2.2 Hz), 130.6, 127.4, 119.2 (d, $J_{C-P}$ = 6.6 Hz), 92.4 (d, $J_{C-P}$ = 54.0 Hz), 82.5 (d, $J_{C-P}$ = 300.3 Hz), 63.3 (d, $J_{C-P}$ = 5.6 Hz), 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −6.31. HRMS $m/z$ (ESI): calcd for $C_{10}H_{13}SO_3P$ $[M + Na]^+$ 267.0221, found 267.0225.

*Diethyl (Pyridin-4-ethynyl)phosphonate (**3p**) (New Compound).* Oil; 91 mg, 76% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.65−8.64 (d, $J$ = 5.5 Hz, 2H), 7.39−7.38 (d, $J$ = 5.5 Hz, 2H), 4.26−4.18 (m, 4H), 1.41−1.37 (t, $J$ = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) $\delta$ 150.1, 125.7 (d, $J_{C-P}$ = 5.3 Hz), 125.9, 94.9 (d, $J_{C-P}$ = 50.6 Hz), 82.8 (d, $J_{C-P}$ = 293.9 Hz), 63.6(d, $J_{C-P}$ = 5.5 Hz), 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −7.52. HRMS $m/z$ (ESI): calcd for $C_{11}H_{14}NO_3P$ $[M + Na]^+$ 262.0609, found 262.0604.

*Diethyl (Naphthalen-2-ylethynyl)phosphonate (**3q**) (New Compound).* Oil; 119 mg, 83% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.10 (s, 1H), 7.82−7.79 (m, 3H), 7.55−7.49 (m, 3H), 4.29−4.21 (m, 4H), 1.43−1.39 (t, $J$ = 7.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 133.8, 132.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.1, 116.7 (d, $J_{C-P}$ = 5.7 Hz), 99.5 (d, $J_{C-P}$ = 53.0 Hz), 78.5 (d, $J_{C-P}$ = 298.4 Hz), 63.3 (d, $J_{C-P}$ = 5.5 Hz), 16.2 (d, $J_{C-P}$ = 7.1 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −6.00. HRMS $m/z$ (ESI): calcd for $C_{16}H_{17}O_3P$ $[M + Na]^+$ 311.0813, found 311.0811.

*Diethyl (Anthracen-9-ylethynyl)phosphonate (**3r**) (New Compound).* Yellow solid; mp 101−102 °C; 149 mg, 88% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.53 (s, 1H), 8.48−8.46 (d, $J$ = 8.6 Hz, 2H), 8.03−8.01 (d, $J$ = 8.5 Hz, 2H), 7.65−7.61 (m, 2H), 7.55−7.51 (d, $J$ = 7.5 Hz, 2H), 4.41−4.32 (m, 4H), 1.50−1.47 (t, $J$ = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 133.8 (d, $J_{C-P}$ = 2.1 Hz), 130.8, 130.7, 129.0, 127.9, 126.0, 125.9, 112.8 (d, $J_{C-P}$ = 5.9 Hz), 96.5(d, $J_{C-P}$ = 52.6 Hz), 89.2 (d, $J_{C-P}$ = 298.1 Hz), 63.4 (d, $J_{C-P}$ = 5.5 Hz), 16.3 (d, $J_{C-P}$ = 7.0 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −5.76. HRMS $m/z$ (ESI): calcd for $C_{20}H_{19}O_3P$ $[M + Na]^+$ 361.0970, found 361.0974.

*(E)-Diethyl (4-Phenylbut-3-en-1-yn-1-yl)phosphonate (**3s**) (New Compound).* Oil; 108 mg, 82% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.38−7.29 (m, 5H), 7.19−7.15 (d, $J$ = 16.3 Hz, 1H), 6.16−6.11 (dd, $J$ = 16.4 Hz, 3.7 Hz, 1H), 4.20−4.12 (m, 4H), 1.37−1.33 (t, $J$ = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 147.3 (d, $J_{C-P}$ = 3.7 Hz), 134.9, 130.0, 128.9, 126.8, 104.5 (d, $J_{C-P}$ = 6.5 Hz), 98.7 (d, $J_{C-P}$ = 52.7 Hz), 80.0 (d, $J_{C-P}$ = 298.8 Hz), 63.1 (d, $J_{C-P}$ = 5.6 Hz), 16.1 (d, $J_{C-P}$ = 7.0 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −5.97. HRMS $m/z$ (ESI): calcd for $C_{14}H_{17}O_3P$ $[M + Na]^+$ 287.0813, found 287.0814.

*Tetraethyl (1,4-Phenylenebis(ethyne-2,1-diyl))bis(phosphonate) (**3t**) (CAS No. 945083-55-1).* 179 mg, 90% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.51 (s, 4H), 4.21−4.13 (m, 4H), 1.37−1.33 (t, $J$ = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 132.6 (d, $J_{C-P}$ = 2.3 Hz), 121.7 (d, $J_{C-P}$ = 5.7 Hz), 97.1 (d, $J_{C-P}$ = 52.5 Hz), 81.3 (d, $J_{C-P}$ = 296.0 Hz), 63.4 (d, $J_{C-P}$ = 5.6 Hz), 16.1 (d, $J_{C-P}$ = 7.1 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −6.82. HRMS $m/z$ (ESI): calcd for $C_{18}H_{24}O_6P_2$ $[M + Na]^+$ 421.0946, found 421.0940.

*Diisopropyl (Phenylethynyl)phosphonate (**3u**) (CAS No. 204009-80-3).* 108 mg, 81% yield. H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.54−7.52 (m, 2H), 7.44−7.40 (m, 1H), 7.37−7.31 (m, 2H), 4.81−4.76 (m, 2H), 1.40−1.37 (dd, $J$ = 6.3 Hz, 2.4 Hz, 12H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 132.5 (d, $J_{C-P}$ = 2.3 Hz), 130.5, 128.5, 119.9 (d, $J_{C-P}$ = 5.3 Hz), 98.1 (d, $J_{C-P}$ = 52.7 Hz), 79.9 (d, $J_{C-P}$ = 299.3 Hz), 72.3 (d, $J_{C-P}$ = 5.6 Hz), 23.9 (d, $J_{C-P}$ = 4.3 Hz), 23.6 (d, $J_{C-P}$ = 4.6 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ −8.59. HRMS $m/z$ (ESI): calcd for $C_{14}H_{19}O_3P$ $[M + Na]^+$ 289.0970, found 289.0964.

*Diphenyl (Phenylethynyl)phosphine Oxide (**3v**) (CAS No. 7608-18-6).* 101 mg, 67% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.91−7.86 (m, 4H), 7.57−7.38 (m, 9H), 7.35−7.30 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 133.7, 132.5 (d, $J_{C-P}$ = 1.6 Hz), 132.2 (d, $J_{C-P}$ = 2.6 Hz), 130.9 (d, $J_{C-P}$ = 11.1 Hz), 130.7, 128.7, 128.6, 119.9 (d, $J_{C-P}$ = 4.1 Hz), 105.5 (d, $J_{C-P}$ = 30.2 Hz), 83.0 (d, $J_{C-P}$ = 168.8 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ 8.18. HRMS $m/z$ (ESI): calcd for $C_{20}H_{15}OP$ $[M + Na]^+$ 325.0758, found 325.0760.

*4-((Diphenylphosphoryl)ethynyl)benzonitrile (**3w**) (CAS No. 58971-88-3).* 123 mg, 75% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.90−7.85 (m, 4H), 7.70−7.65 (m, 4H), 7.60−7.56 (m, 2H), 7.53−7.48 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 133.0 (d, $J_{C-P}$ = 1.5 Hz), 132.6 (d, $J_{C-P}$ = 2.7 Hz), 132.3 (d, $J_{C-P}$ = 122.2 Hz), 132.2, 131.0 (d, $J_{C-P}$ = 11.2 Hz), 128.8 (d, $J_{C-P}$ = 13.6 Hz),124.7 (d, $J_{C-P}$ = 3.9 Hz), 117.8, 114.1, 102.3 (d, $J_{C-P}$ = 28.5 Hz), 87.1 (d, $J_{C-P}$ = 162.1 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ 8.40. HRMS $m/z$ (ESI): calcd for $C_{21}H_{14}ONP$ $[M + Na]^+$ 350.0711, found 350.0706.

*(Naphthalen-2-ylethynyl)diphenylphosphine (**3x**) (CAS No. 930807-33-3).* 144 mg, 82% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.16 (s, 1H), 7.97−7.91 (m, 4H), 7.85−7.82 (m, 3H), 7.60−7.48 (m, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 133.9, 133.8, 133.7 (d, $J_{C-P}$ = 2.0 Hz), 132.6, 132.5 (d, $J_{C-P}$ = 2.8 Hz), 131.0 (d, $J_{C-P}$ = 11.2 Hz), 128.7 (d, $J_{C-P}$ = 13.3 Hz), 128.4, 128.1, 128.0, 127.9, 127.8, 127.1, 117.1 (d, $J_{C-P}$ = 4.2 Hz), 105.9 (d, $J_{C-P}$ = 29.7 Hz), 83.1 (d, $J_{C-P}$ = 169.4 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ 6.44. HRMS $m/z$ (ESI): calcd for $C_{24}H_{17}OP$ $[M + Na]^+$ 375.0909, found 375.0903.

*Ethyl Phenyl(phenylethynyl)phosphinate (**3y**) (CAS No. 225928-24-5).* 108 mg, 80% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.97−7.91 (m, 2H), 7.59−7.47 (m, 5H), 7.44−7.40 (m, 1H), 7.36−7.32 (m, 2H), 4,32−4.25 (m, 2H), 1.44−1.40 (t, $J$ = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 132.8 (d, $J_{C-P}$ = 2.9 Hz), 132.6 (d, $J_{C-P}$ = 2.0 Hz), 131.2 (d, $J_{C-P}$ = 165.8 Hz), 131.1 (d, $J_{C-P}$ = 11.2 Hz), 130.6, 128.6 (d, $J_{C-P}$ = 14.9 Hz), 119.8 (d, $J_{C-P}$ = 4.2 Hz), 101.5 (d, $J_{C-P}$ = 39.7 Hz), 81.8 (d, $J_{C-P}$ = 216.1 Hz), 62.3 (d, $J_{C-P}$ = 6.4 Hz), 16.4 (d, $J_{C-P}$ = 7.0 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ 9.93. HRMS $m/z$ (ESI): calcd for $C_{16}H_{15}O_2P$ $[M + Na]^+$ 293.0707, found 293.0703.

*Ethyl (Naphthalen-1-ylethynyl)(phenyl)phosphinate (**3z**) (CAS No. 225928-24-5).* 133 mg, 83% yield. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.23−8.21 (d, $J$ = 8.3 Hz, 1H), 8.06−8.00 (m, 2H), 7.91−7.89 (d, $J$ = 8.3 Hz, 1H), 7.85−7.83 (d, $J$ = 7.6 Hz, 1H), 7.80−7.79 (d, $J$ = 7.0 Hz, 1H), 7.61−7.49 (m, 5H), 7.44−7.40 (t, $J$ = 7.9 Hz, 1H), 4.41−4.33 (m, 2H), 1.48−1.44 (t, $J$ = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 133.3, 132.9, 132.8 (d, $J_{C-P}$ = 2.7 Hz), 132.6 (d, $J_{C-P}$ = 2.0 Hz), 131.4 (d, $J_{C-P}$ = 165.6 Hz), 131.3, 131.2 (d, $J_{C-P}$ = 11.7 Hz), 128.7, 128.6, 127.7, 126.9, 125.6, 125.0, 117.1 (d, $J_{C-P}$ = 4.4 Hz), 100.1 (d, $J_{C-P}$ = 39.5 Hz), 86.5 (d, $J_{C-P}$ = 214.0 Hz), 62.4 (d, $J_{C-P}$ = 6.4 Hz), 16.5 (d, $J_{C-P}$ = 6.9 Hz). $^{31}P$ NMR (162 MHz, $CDCl_3$): $\delta$ 9.67. HRMS $m/z$ (ESI): calcd for $C_{20}H_{17}O_2P$ $[M + Na]^+$ 343.0864, found 343.0856.

## ■ ASSOCIATED CONTENT

### Supporting Information

Copies of $^1H$ NMR, $^{31}P$ NMR, and $^{13}C$ NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.


dx.doi.org/10.1021/jo500312n | J. Org. Chem. 2014, 79, 3678−3683

## AUTHOR INFORMATION


### Corresponding Authors

*E-mail: gaoxingchem@xmu.edu.cn.
*E-mail: stacyliu@xmu.edu.cn.


### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This work was supported by the Chinese National Natural Science Foundation (21202135), the Natural Science Foundation of Fujian Province of China (Nos. 2013J05031 and 2012J01053), and the National Basic Research Program of China (2012CB821600).

## REFERENCES


(1) Some selected publications: (a) Iorga, B.; Eymery, F.; Carmichael, D.; Savignac, P. *Eur. J. Org. Chem.* **2000**, 3103−3115 and references cited therein. (b) Ashburn, B. O.; Carterand, R. G.; Zakharov, L. N. *J. Am. Chem. Soc.* **2007**, *129*, 9109−9116. (c) Nishida, G.; Noguchi, K.; Hirano, M.; Tanaka, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 3951−3954. (d) Kee, J. M.; Villani, B.; Carpenter, L. R.; Muir, T. W. *J. Am. Chem. Soc.* **2010**, *132*, 14327−14329. (e) Kettles, T. J.; Cockburn, N.; Tam, W. *J. Org. Chem.* **2011**, *76*, 6951−6957. (f) Li, X. B.; Hu, G. B.; Luo, P.; Tang, G.; Gao, Y. X.; Xu, P. X.; Zhao, Y. F. *Adv. Synth. Catal.* **2012**, *354*, 2427−2432. (g) Kocsis, L. S.; Benedetti, E.; Brummond, K. M. *Org. Lett.* **2012**, *12*, 4430−4433. (h) Mo, J.; Kang, D. J.; Eom, D.; Kimand, S. H.; Lee, P. H. *Org. Lett.* **2013**, *15*, 26−29.

(2) Lera, M.; Hayes, C. J. *Org. Lett.* **2000**, *2*, 3873−3875.

(3) Selected recent publications: (a) Gao, Y. X.; Wang, G.; Chen, L.; Xu, P. X.; Zhao, Y. F.; Zhou, Y. B.; Han, L. B. *J. Am. Chem. Soc.* **2009**, *131*, 7956−7957. (b) Liu, P.; Yang, J.; Li, P. H.; Wang, L. *Appl. Organomet. Chem.* **2011**, *25*, 830−835. (c) Bernoud, E.; Alayrac, C.; Delacroix, O.; Gaumont, A. C. *Chem. Commun.* **2011**, *47*, 3239−3241. (d) Jouvin, K.; Heimburger, J.; Evano, G. *Chem. Sci.* **2012**, *3*, 756−760. (e) Jouvin, K.; Veillard, R.; Theunissen, C.; Alayrac, C.; Gaumont, A. C.; Evano, G. *Org. Lett.* **2013**, *15*, 4592−4595.

(4) (a) Hu, J.; Zhao, N.; Yang, B.; Wang, G.; Guo, L. N.; Liang, Y. M.; Yang, S. D. *Chem.—Eur. J.* **2011**, *17*, 5516−5521. (b) Li, X.; Yang, F.; Wu, Y. J.; Wu, Y. S. *Org. Lett.* **2014**, *16*, 992−995.

(5) (a) Honga, J. E.; Leea, C. W.; Kwona, Y.; Oha, D. Y. *Synth. Commun.* **1996**, *26*, 1563−1567. (b) Lecerclé, D.; Mothes, C.; Taran, F. *Synth. Commun.* **2007**, *37*, 1301−1311. (c) Yatsumonji, Y.; Ogata, A.; Tsubouchi, A.; Takeda, T. *Tetrahedron Lett.* **2008**, *49*, 2265−2267.

(6) Leadbeater, N. E.; Marco, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 1407−1409.

(7) (a) Chelucci, G. *Chem. Rev.* **2012**, *112*, 1344−1362 and references cited therein. (b) Liu, J.; Li, P. H.; Chen, W.; Wang, L. *Chem. Commun.* **2012**, *48*, 10052−10054. (c) Chen, L.; Puniredd, S. R.; Tan, Y. Z.; Baumgarten, M.; Zschieschang, U.; Enkelmann, V.; Pisula, W.; Feng, X. L.; Klauk, H.; Mullen, K. *J. Am. Chem. Soc.* **2012**, *134*, 17869−17872. (d) Huang, Z.; Shang, R.; Zhang, Z. R.; Tan, X. D.; Xiao, X.; Fu, Y. *J. Org. Chem.* **2013**, *78*, 4551−4557.

(8) (a) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, *13*, 3769−3772. (b) Uenishi, J.; Kawahama, R.; Yonemitsu, O.; Tsuji, J. *J. Org. Chem.* **1998**, *63*, 8965−8975.

(9) Some selected publications: (a) Zapata, A. J.; Ruiz, J. *J. Organomet. Chem.* **1994**, *479*, C6−C8. (b) Shen, W.; Wang, L. *J. Org. Chem.* **1999**, *64*, 8873−8879. (c) Olivo, H. F.; Velazquez, F.; Trevisan, H. C. *Org. Lett.* **2000**, *2*, 4055−4058.

(10) (a) Coste, A.; Karthikeyan, G.; Couty, F.; Evano, G. *Angew. Chem.* **2009**, *121*, 4445−4449. (b) Coste, A.; Couty, F.; Evano, G. *Org. Lett.* **2009**, *11*, 4454−4457.

(11) Jouvin, K.; Bayle, A.; Legrand, F.; Evano, G. *Org. Lett.* **2012**, *14*, 1652−1655.

(12) (a) Evano, G.; Tadiparthi, K.; Couty, F. *Chem. Commun.* **2011**, *47*, 179−181. (b) Liu, L.; Wang, Y. L.; Zeng, Z. P.; Xu, P. X.; Gao, Y. X.; Yin, Y. W.; Zhao, Y. F. *Adv. Synth. Catal.* **2013**, *355*, 659−666.

(13) (a) Hirao, T.; Masunaga, T.; Ohshiro, Y.; Agawa, T. *J. Org. Chem.* **1981**, *46*, 3745−3747. (b) Abbas, S.; Hayes, C. J.; Worden, S. *Tetrahedron Lett.* **2000**, *41*, 3215−3219. (c) Kuang, C.; Senboku, H.; Tokuda, M. *Tetrahedron* **2002**, *58*, 1491−1496.

(14) (a) Zhang, X. H.; Liu, H. Z.; Hu, X. M.; Tang, G.; Zhu, J.; Zhao, Y. F. *Org. Lett.* **2011**, *13*, 3478−3481. (b) Zhao, Z. X.; Xue, W. H.; Gao, Y. X.; Tang, G.; Zhao, Y. F. *Chem.—Asian J.* **2013**, *8*, 713−716. (c) Hu, G. B.; Chen, W. Z.; Fu, T. T.; Peng, Z. M.; Qiao, H. W.; Gao, Y. X.; Zhao, Y. F. *Org. Lett.* **2013**, *15*, 5362−5365.

(15) Some selected publications: (a) Buchwald, S.; Bolm, C. *Angew. Chem., Int. Ed.* **2009**, *48*, 5586−5587. (b) Crabtree, R. H. *Chem. Rev.* **2012**, *112*, 1536−1554. (c) Thomé, I.; Nijs, A.; Bolm, C. *Chem. Soc. Rev.* **2012**, *41*, 979−987. (d) Bhunia, A.; Yetra, S. R.; Biju, A. T. *Chem. Soc. Rev.* **2012**, *41*, 3140−3152.

(16) (a) Tavs, P. *Chem. Ber.* **1970**, *103*, 2428−2432. (b) Tavs, P.; Weitkamp, H. *Tetrahedron* **1970**, *26*, 5529−5534. (c) Thomé, I.; Nijs, A.; Bolm, C. *Chem. Soc. Rev.* **2012**, *41*, 979−987. (d) Rajeshwaran, G. G.; Nandakumar, M.; Sureshbabu, R.; Mohanakrishnan, A. K. *Org. Lett.* **2011**, *13*, 1270−1273.

(17) (a) Li, P.; Alper, H. *J. Org. Chem.* **1986**, *51*, 4354−4356. (b) Okutani, M.; Mori, Y. *J. Org. Chem.* **2009**, *74*, 442−444.

(18) (a) Arbuzov, B. A. *Pure Appl. Chem.* **1964**, *9*, 307−336. (b) Bhattacharya, A. K.; Thyagarajan, G. *Chem. Rev.* **1981**, *81*, 415−430.