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Selective hydrophosphorylation of alkynes for the synthesis of (*E*)-vinylphosphonates†

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Hydrophosphorylation of alkynes with dialkylphosphites in the various copper catalysts was investigated. The reactions provided the regio- and stereoselective *E*-vinylphosphonates under commercially available copper chloride catalyst in the presence of ethylene diamine as an efficient ligand. The impact of solvents, temperature, and diamine ligands are included in this report. In addition, the DFT calculations provided insight into the regio- and stereoselectivity of the reaction. It is suggested that the reaction proceeded *via* an *in situ* generated $Cu(AN)_4^+$ complex. The reaction of phenylacetylene with diethyl phosphite in the presence of EDA and the $(CH_3CN)_4CuBF_4$ complex as a catalyst also gave the corresponding *E*-vinylphosphonates in good yield.

Introduction

Transition metal-catalyzed carbon–phosphorus (C–P) bond formation is one of the most straightforward ways for the synthesis of various organophosphorus compounds.[1–5] One of the important and atom-economical approaches for the carbon–phosphorus bond formation is transition metal-catalyzed addition of P–H bonds to alkynes for the synthesis of alkenylphosphine oxides and vinylphosphonates, which have wide applications in organic synthesis and industrial processes.[6–10] Several metal-catalyzed C–P bond formation methods have been reported for the synthesis of alkenylphosphine oxides *via* addition reaction of $R_2P(O)H$ compounds to alkynes, including palladium,[11] nickel,[12] rhodium,[13] ytterbium complex,[14] and copper salts.[15] However, in contrast to $R_2P(O)H$, hydrophosphorylation of alkynes with dialkylphosphite $[(RO)_2P(O)H]$ for the synthesis of highly selective vinylphosphonates (Markovnikov and anti-Markovnikov addition and also *E*/*Z*-selectivity) is still hot research topic. The first palladium and nickel-catalyzed addition of dialkyl phosphite $[(RO)_2P(O)H]$ to alkynes was reported by Tanaka and Han to give a mixture of non-selective corresponding vinylphosphonates.[16] In spite some significant achievements in the palladium- and nickel-catalyzed addition of dialkylphosphite to alkynes, the drawbacks of the catalyst systems, such as sensitivity of complexes to air, high cost, low selectivity and toxicity, limit their applications.

Three different research groups developed copper-catalyzed additions of $R_2P(O)H$ compounds to alkynes for the synthesis of alkenylphosphine oxides under copper catalyst system.[15,17,18]

In continuing our efforts for the synthesis of organophosphorus compounds,[19] we recently reported a convenient preparation of vinylphosphonates *via* chemo- and stereoselective Knoevenagel condensation reaction of carbonyl compounds with cyanomethylphosphonate.[20] Herein, a simple copper-catalyzed hydrophosphorylation of alkynes with dialkylphosphite was reported for the regio- and stereoselective synthesis of *E*-vinylphosphonates. In addition, in order to reveal the details of the regio- and stereoselectivity of the reaction, the proposed mechanism was also studied using DFT method of calculation.

Results and discussion

Initially, the reaction of phenylacetylene **1a** with diethyl phosphite was examined as the model reaction. The results screening of various reaction conditions are shown in Table 1. No reaction was observed when $Cu(OAc)_2$, $Pd(OAc)_2$, and $FeCl_3$ were used as a catalyst in the presence of ethylenediamine (EDA) in acetonitrile at reflux for 24 h (entries 1–3). Upon using $CuCl_2$ a mixture of products was obtained in a low yield after 24 h (entry 4). When the reaction was conducted with CuCl (10 mol%) in acetonitrile for 24 h, the compound **2a** was obtained in 42% yield (entry 5). No catalytic activities were observed with CuBr and CuI (entries 6 and 7). It seems that CuCl has better activity in the presence of EDA. The results for the reactions conducted in various solvents showed that no reaction was observed when CH_2Cl_2, DMF, or DMSO were used as a solvent (entries 8–10), while using dioxane, the compound **2a**

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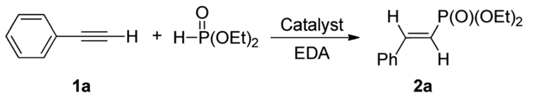
† Electronic supplementary information (ESI) available: Characterization data for all the compounds **2a–2y** and copies of ^{1}H NMR and ^{13}C NMR, and ^{31}P NMR of all products. See DOI: https://doi.org/10.1039/d5ra00300h

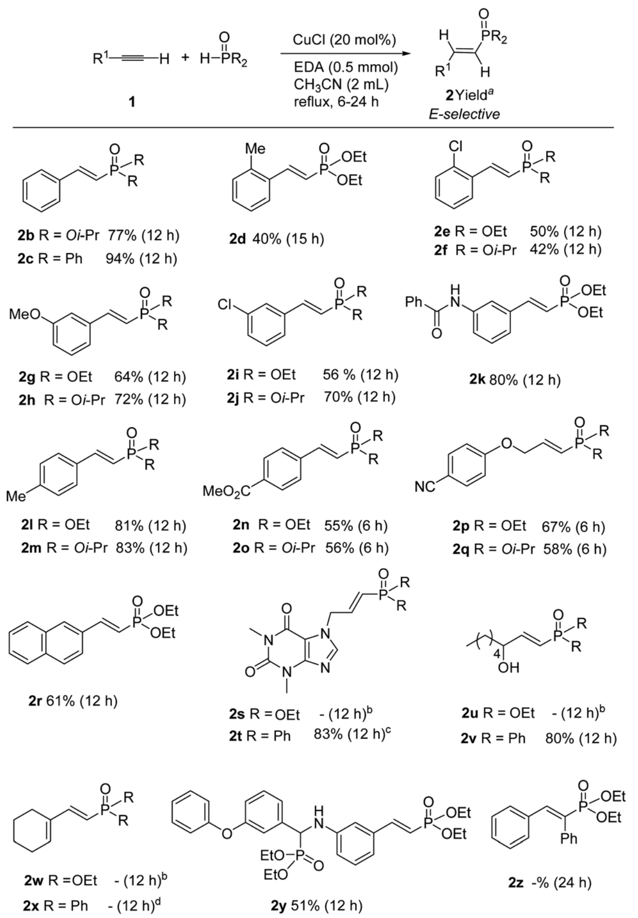
Table 1 Catalytic hydrophosphorylation of phenylacetylene **1a** with diethylphosphite under various conditions



Entry	Catalyst	Solvent	T (°C)	Time (h)	Yield of 2[a] (%)
1	$Cu(OAc)_2$	MeCN	Reflux	24	—
2	$Pd(OAc)_2$	MeCN	Reflux	24	—
3	$FeCl_3$	MeCN	Reflux	24	—
4	$CuCl_2$	MeCN	Reflux	24	—[b]
5	CuCl	MeCN	Reflux	24	42
6	CuBr	MeCN	Reflux	24	—
7	CuI	MeCN	Reflux	24	—
8	CuCl	CH_2Cl_2	Reflux	24	—
9	CuCl	DMSO	90	24	—
10	CuCl	DMF	90	24	—
11	CuCl	Dioxane	90	24	24[c]
12	CuCl	MeCN	Reflux	24	89[d]
13	CuCl	MeCN	Reflux	12	89[d]
14	CuCl	MeCN	Reflux	4	35[d]
15	CuCl	MeCN	rt	48	—[d]
16	CuCl	MeCN	Reflux	24	53[d,e]
17	CuCl	MeCN	Reflux	24	41[d,f]
18	CuCl	MeCN	Reflux	24	83[d,g]

[a] Yield refers to the isolated pure product **2a** after short column chromatography on silica-gel for the reaction of **1a** (2.0 mmol) with diethylphosphite (1 mmol) in the presence of EDA (0.5 mmol) and catalyst (10 mol%). [b] Mixture of products were detected. [c] Has an E/Z ratio of 80 : 20. [d] CuCl (20 mol%). [e] 1,2-Cyclohexyldiamine (0.5 mmol) as a ligand. [f] Ammonia solution (0.5 mL, 25%) was added instead of EDA. [g] Reaction carried-out under Ar.

Table 2 Catalytic hydrophosphorylation of phenylacetylene **1a** with phosphite and phosphine oxide in the presence of EDA and CuCl



[a] Yield refers to the isolated pure product **2** after short column chromatography on silica gel. [b] The reaction failed to give any addition product after 12. [c] E/Z ratio is 90 : 10 (based on ^{31}P NMR). [d] Mixture of unidentified compounds was formed.

was obtained in only 24% in moderate selectivity (entry 11). To improve the reaction yield, the effects of the amount of CuCl, the reaction time, ligand, and temperatures were investigated (entries 12–17). Interestingly, when the reaction was conducted with increasing the amount of the CuCl to 20 mol%, the compound **2a** was obtained in 89% yield (entry12). It is worthy to note that the reaction proceeds to give the product **2a** in 89% yield for 12 h (entry 13). When the reaction was carried out at reflux for 4 h, the reaction yield was decreased to 35% (entry 14). No reaction was observed when the reaction was carried out in the presence of EDA in acetonitrile at rt for 48 h (entries 15). When 1,2-diamino cyclohexane was taken in place of ethylenediamine during the reaction, the compound **2a** was obtained in 53% yield with lower selectivity (entry 16). The reaction in the presence of ammonia solution also proceeded and the compound **2a** was obtained in 41% yield (entry 17). When the reaction was carried out at reflux for 24 h under Ar, the reaction yield was slightly decreased to 83% (entry 18).

With the optimized conditions in hands, next we examined the synthetic scope of the reaction. As shown in Table 2, the present reaction was successfully applied to a wide range of alkynes. The results showed that the electronic nature of the aryl group in aromatic alkyne **1** did not affect the reaction outcome significantly (**2a–2w**). It should be noted that alkynes with amide (**1k**), ester (**1n**), and nitrile (**1p**), group gave the desired products without any side products. The reaction of 2-naphthylacetylene **1r** with diethylphosphite in the presence of EDA and CuCl (20 mol%) gave the desired product **2r** in moderate yield. Treatment of heterocyclic alkyne **1s** with a mixture of diphenylphosphine oxide, EDA and CuCl (20 mol%) for 12 h gave the corresponding product **2t** in good yield with 90 : 10 of E/Z ratio based on ^{31}P NMR analysis. The reactions of aliphatic substrate **1u** also gave the desired product **2v** in good yield. Treatment of alkyne **1y**, an aminophosphonate derivative, with a mixture of diethyl phosphite, EDA and CuCl (20 mol%) for 12 h gave the corresponding product **2y** in good yield. It should be noted that the internal alkyne, diphenylacetylene, failed to give any addition product (**2z**) after 24 h.

To gain insights into the mechanism, several control experiments were carried out. The reaction of alkyne with diethylphosphite in the presence of CuCl without the addition of EDA was conducted; however, no product was observed. In other experiment, when the reaction was carried out in the absence of diethylphosphite, an alkyne homo-coupling product **3** was obtained in 90% yield (Scheme 1). In the next trial, the influence of EDA on the reaction efficiency was also examined in the absence of diethylphosphite. As a result, the yield of **3** was decreased to 10% in the absence of EDA. Thus, it was confirmed that the EDA has major role in the conversion.

Furthermore, the nature of reaction mixture is revealed by NMR-spectroscopy. The ^{1}H NMR spectrum of the reaction mixture without further purification was shown in Fig. 1. As shown in Fig. 1, the olefinic proton signal appearing as doublets at 5.95 and 6.72 ppm with a *J*-value of 12.0 Hz confirmed the presence of *Z* or *cis*-configuration of double bonds and doublets at 6.41 and 7.08 ppm with a *J*-value of 16.0 Hz confirmed the presence of *E* or *trans*-configuration of self-addition adduct of alkyne **1a** in the reaction condition.[21] The isolation as the individual pure alkene side products by chromatography was not unfortunately successful due to their very similar polarities on a stationary phase of silica-gel.

To find insights for the reaction outcome, we evaluated the reaction paths from cationic species bearing a dimethyl phosphonate moiety to yield *E*- and *Z*-products by the DFT calculations at B3LYP/LACVP++** level of theory (Fig. 2 and 3). In the first step, phenylacetylene, **A**, and tetrakis(acetonitrile) copper(I) complex, **AN$_4$Cu**, produces a copper alkyne complex, **AN$_3$CuA**. Due to low electrostatic and Mulliken charges on the Cu atom and the steric effect of the coordinated dimethylphosphite, **P′**, of the **AN$_3$CuP′** complex, the reaction is preferred to start by the attack of **A** as nucleophile at the electrophilic Cu atom of the **AN$_4$Cu** complex (Fig. 2). The main tetrahedral Cu(I) complex, **AN$_2$CuAP′**, that contains both reactive species is formed by the attack of **P′** on the centre of copper π-complex, **AN$_3$CuA**. **P′** that is 3.1 kcal mol^{-1} less stable than its tautomer, **P**, can act as a nucleophile. The complex formation constants for aqueous copper(I) ion with halide ions and acetonitrile (AN) as ligand are as follow: $I^- > Br^- > Cl^- >$ AN. Therefore, the formation of $Cu(AN)_4^+$ complex in the presence of I^- and Br^- ions is more inhibited than that of Cl^- ion.[22] It should be noted that the reaction of **1a** with diethylphosphite in the presence of EDA and the $(CH_3CN)_4CuBF_4$ complex as a catalyst gave the compound **2a** in 85% yield (see Fig. S74†). Many of the dialkyl phosphite reactions appear to progress *via* its minor tautomer.[23] The reaction is proceded by the formation of a metal σ-complex, **σ-Cpx**, *via* π-σrearrangement of the organocopper π-complex, **π-Cpx**. The reaction occurred by the addition of ethylene diamine, **EDA**. During the reaction process, the **σ-Cpx** intermediate is converted into the ***E*-Pdt** *via* an intramolecular proton transfer reaction. The *syn*-periplanar conformation of the hydroxyl group with Cu is required for this 1,4-prototropic mechanism (Scheme 2). The ***Z*-σ-Cpx** intermediate is only formed from the rearrangement of **π-Cpx** to **σ-Cpx** *via* the stereospecific *syn*-addition of Cu–P bond to the C–C triple bond. The ***E*-Pdt** is created in the rate determining step of the reaction. An energy barrier of about 22.6 kcal mol^{-1} limits the formation of the product at the fourth step (Fig. 3). Based-on this result, the reaction is expected to proceed at temperatures a little above 25 °C. Therefore, the reaction is enthalpically favoured and ***E*-Pdt** is the only product of the highly regioselective reaction.

The solvent effect is addressed by the comparison between the energy profile of the reaction in the gas and acetonitrile phases determined at the same level of theory (Fig. 3). The results obviously show that the reaction speed down in the solution phase at room temperature.

In summary, herein we reported a novel approach for the regio and stereoselective synthesis of *E*-vinylphosphonates *via* a selective hydrophosphorylation of alkynes in copper chloride catalyst in the presence of EDA as an efficient ligand at reflux. Results showed that the CuClin acetonitrile in the presence of EDA is a convenient and effective catalyst for the selective hydrophosphorylation of alkynes. It is suggested that the reaction proceeded *via* an **AN$_3$CuP′** complex in EDA media. Stereochemistry of the *E*-isomer was determined by careful NMR

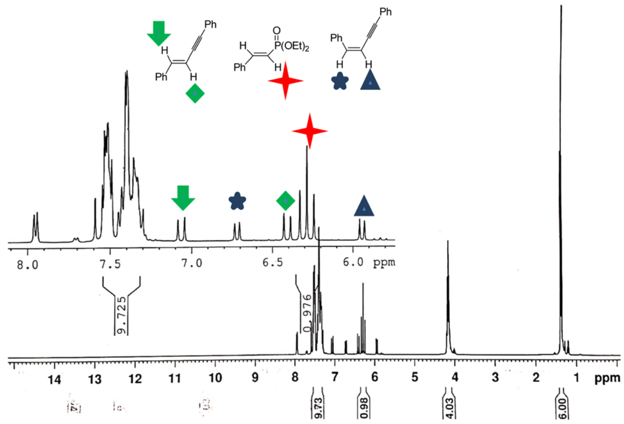


Fig. 1 ^{1}H NMR spectrum of the reaction mixture of **1a** in $CDCl_3$.

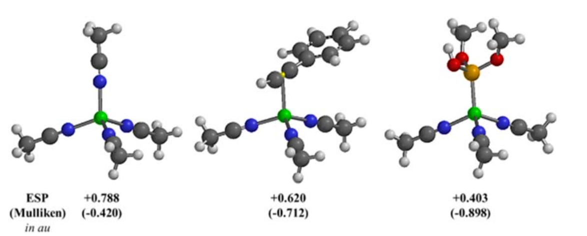
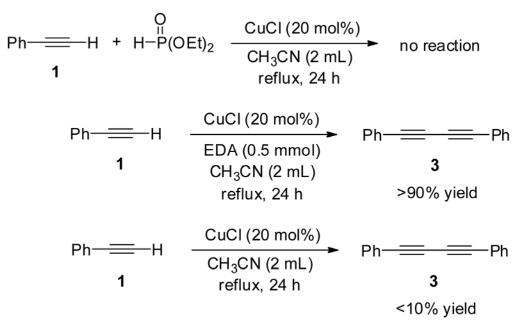


Fig. 2 The electrostatic (ESP) and Mulliken charges of the Cu atom in the starting complexes; from left to right: AN$_4$Cu, AN$_3$CuA and AN$_3$CuP′.



Scheme 1 Control reactions.

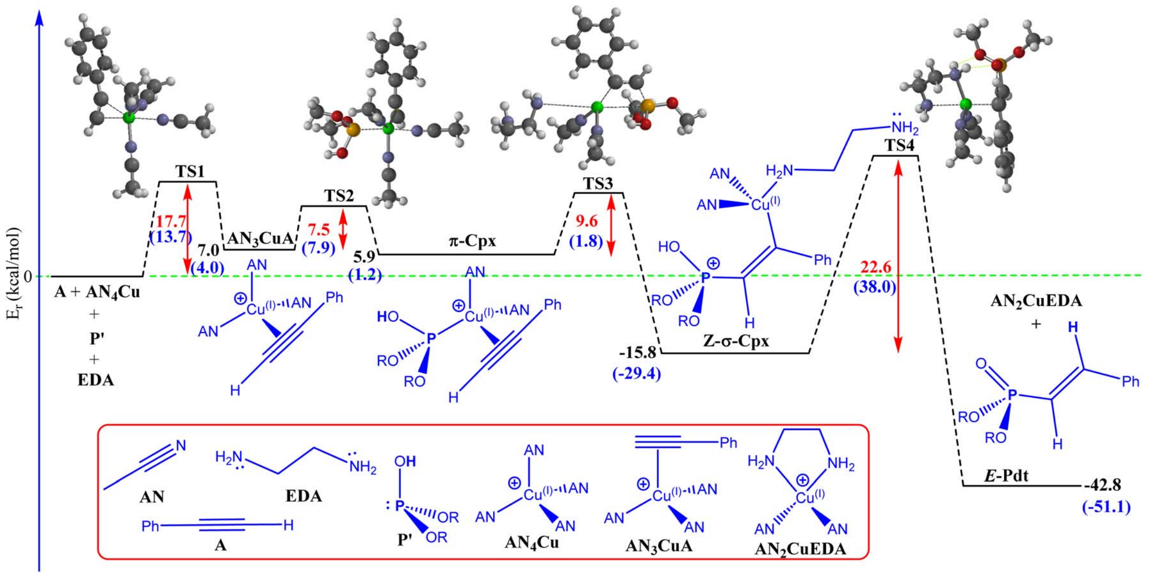
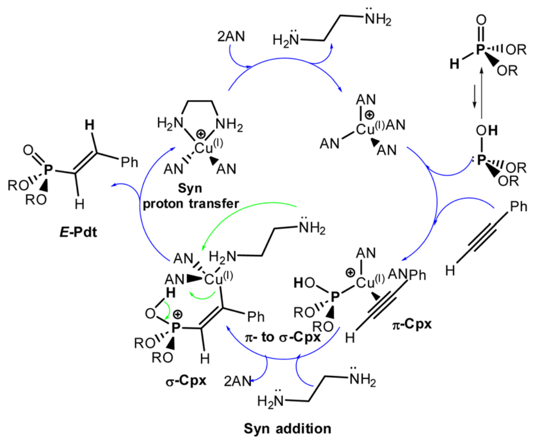


Fig. 3 Energy profile for the reaction in gas phase and in acetonitrile solution (the number in parentheses), calculated at the B3LYP/LACVP++** level of theory at 298.1.



Scheme 2 Plausible reaction mechanism for the highly regio- and stereoselective synthesis of *E*-Pdt.

analysis. To understand the selectivity of the reaction, DFT calculations have provided insight into the basis of these reactivity and selectivity.

Experimental

General methods

All chemicals were commercial products. CuCl (Merck, Art. No. 102739) was purchased from commercial distributors and used as received. NMR spectra were obtained with a 400 MHz Bruker Avance instrument with the chemical shifts being reported as δ ppm and couplings expressed in hertz. The chemical shift data for each signal on ^{1}H NMR are given in units of δ relative to $CHCl_3$ ($\delta = 7.26$) for $CDCl_3$ solution. For ^{13}C NMR spectra, the chemical shifts in $CDCl_3$ and DMSO are recorded relative to the $CDCl_3$ resonance ($\delta = 77.0$) and DMSO resonance ($\delta = 40.45$). Silica gel column chromatography was carried out with silica gel 100 (Merck No. 10184). Merck silica-gel 60 F254 plates (No. 5744) were used for the preparative TLC.

Procedure for the synthesis of *N*-(3-ethynylphenyl) benzamide (1k). The compound **1k** was obtained according to the literature report with slight modification.[24] TEA was added to a solution of 3-ethynylaniline (351 mg, 3 mmol) in DCM (14 mL) and the mixture was stirred for 15 min at ar. Benzoyl chloride (3 mmol) was added drop by drop to the mixture and the mixture was stirred for 2 hours at rt. After the completion of the reaction, the reaction mixture was washed with water (2 × 5 mL) and the crude product was obtained after evaporation of the organic phase. Finally the desired amide **1k** was obtained as a pure crystal after recrystallization from EtOAc/*n*-hexane.

*N-(3-Ethynylphenyl)benzamide (**1k**).* The product was obtained as white solid 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.91–7.78 (m, 3H), 7.75–7.68 (m, 1H), 7.61–7.42 (m, 3H), 7.31 (dd, $J = 7.8$, 4.4 Hz, 2H), 3.11 (s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 166.1, 138.0, 134.7, 132.0, 129.10, 128.8, 128.3, 127.1, 123.8, 122.9, 121.0, 83.2.

Procedure for the synthesis of 4-cyanophenoxy propargyl ether 1p. The compound **1p** was obtained according to the literature report with slight modification.[25] 4-Cyanophenol (3.5 mmol) was added to a mixture of K_2CO_3 (7.2 mmol) in dry DMF (22 mL) and the mixture was stirred for 15 min at 80 °C. Propargyl bromide (3.9 mmol) was added to the reaction mixture and the mixture was stirred for 12 h at 80 °C. After completion of the reaction (12 h), the mixture was diluted with water (50 mL) and extracted with diethyl ether (3 × 50). The organic phase was washed with brine and dried over sodium sulfate. The pure product was obtained by column chromatography over silica gel.

Procedure for the synthesis of 1,3-dimethyl-7-(prop-2-yn-1-yl)-3,7-dihydro-1*H*-purine-2,6-dione (1s). The compound **1s** was obtained according to the literature report with slight modification.[26] Potassium carbonate (1.9 g, 14.4 mmol) was added to a solution of theophylline 1 (2 g, 11.1 mmol) in DMF (30 mL) and the mixture was stirred for 20 min at rt. Propargyl bromide (1.68 mL, 22.2 mmol) was added to the reaction mixture at rt and the mixture was stirred for 2 h at 85 °C. The reaction mixture was cooled to 0 °C, water was added and a solid was precipitated. The formed solid was filtered and dried to afford compound **1s** (2.2 g, 91%) as an off-white solid.

*1,3-Dimethyl-7-(prop-2-yn-1-yl)-3,7-dihydro-1H-purine-2,6-dione (**1s**).* ^{1}H NMR (400 MHz, DMSO): δ 8.20 (s, 1H), 5.19 (d, J = 2.6 Hz, 2H), 3.58 (t, J = 2.6 Hz, 1H), 3.44 (s, 3H), 3.25 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, DMSO): δ 154.7, 151.5, 148.8, 142.6, 106.2, 79.7, 78.4, 77.3, 36.2, 29.9.

Procedure for the synthesis of diethyl(((3-ethynylphenyl)amino)(3-phenoxyphenyl)methyl)phosphonate (1y). The compound **1y** was obtained according to the literature report with slight modification.[27] 3-Phenoxybenzaldehyde (810 mg, 4.1 mmol) was added to a mixture of 3-ethynylaniline (468 mg, 4 mmol) and diethyl phosphite (621 mg, 4.5 mmol) in 1,4-dioxane (12 mL). The reaction mixture was stirred at 60 °C for 7 h. The mixture was then diluted with water (50 mL) and extracted with diethyl ether (3 × 50 mL). The organic phase was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The crude product was purified by column chromatography over silica gel.

Diethyl(((3-ethynylphenyl)amino)(3-phenoxyphenyl)methyl)phosphonate 1y. The product was obtained as gray solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.28 (m, 3H), 7.24 (m, 1H), 7.11 (s, 3H), 7.00–6.86 (m, 4H), 6.74 (dd, J = 2.5, 1.4 Hz, 1H), 6.61 (m, 1H), 4.75 (d, J = 24.4 Hz, 1H), 4.25–3.68 (m, 4H), 3.03 (s, 1H), 1.32 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.45 (d, J = 2.7 Hz), 156.98, 146.04 (d, J = 14.8 Hz), 137.66, 130.07 (d, J = 2.6 Hz), 129.80, 129.20, 123.37, 122.73, 122.66, 122.51, 118.82, 118.47 (d, J = 3.2 Hz), 118.36 (d, J = 5.4 Hz), 117.15, 114.80, 83.95, 63.47 (d, J = 7.0 Hz), 56.44, 54.94, 16.4 (d, J = 5.8 Hz), 16.3 (d, J = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.78 ppm.

General procedure for the hydrophosphorylation of alkynes. Alkyene **1** (1 mmol) was added to a mixture of dialkyl phosphite or diphenylphosphine oxide (2.2 mmol) and CuCl (20 mol%) in acetonitrile (2.5 mL) in the presence of ethylene diamine (0.6 mmol). The reaction mixture was stirred at reflux for 6–24 h without using any inert gas. The completion of the reaction was monitored by TLC. Ethyl acetate (10 mL) was added to the reaction mixture and the solution was washed with water (2 × 5 mL) and dried over sodium sulfate. The solvent was evaporated and the crude product was purified by a short column chromatography with *n*-hexane–EtOAc (5 : 1 to 1 : 5) to give the compound **2** as the viscous oil or white solid. All products gave satisfactory spectral data in accord with the assigned structures.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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