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# ω-Alkyne-Mono- and Diphosphonates – Synthesis and Sonogashira Cross-Coupling Reaction with Aryl Halides

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**Keywords:** Alkynes / Cross-coupling / N ligands / Phosphonates

A convergent approach to functionalise aromatic compounds with a linker terminated by a phosphonate group is reported. The starting point of this strategy is the synthesis of five new ω-alkyne-phosphonates. The linker between the phosphonate group and the alkyne part is either an alkyl or an ether chain. This strategy is based on the use of the phosphonate group as the anchoring point for the attachment of organic compounds onto alumina and the alkyne group, which is used to functionalise aryl halide compounds by a Sonogashira cross-coupling. The use of 1,10-phenanthroline as substrate illustrates the application of this strategy to an aromatic ligand.
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## Introduction

In recent years, the immobilisation of homogeneous catalysts has received a considerable amount of attention.[1] This approach dramatically reduces the difficulties associated with the separation of the catalyst from the reaction media, which is also the first step of the catalyst recycling. The immobilisation step affords also a possibility to isolate the catalytic sites that can, sometimes, enhance the catalytic activity.[2] The support, which can be composed of a variety of different materials (organic, bioorganic, inorganic or hybrid), can act as either a "spectator" in the course of a reaction or, on the contrary, play an important role in the selectivity of the reaction. As an illustration of the influence of the support on the selectivity, the immobilisation of an achiral catalyst (coordination complexes) onto an enzyme by T.R. Ward and coworkers demonstrates that the second sphere of coordination (in that case the enzymatic support) is able to achieve high chiral induction.[3] Whatever the nature of the support, the immobilised molecules need at least one anchoring point and sometimes a spacer between the point of attachment and the molecule (ligand) subjected to immobilisation. The nature of the anchoring functionality is imposed by the nature of the support used. It can be a polymerisable species, for immobilisation by polymerisation or copolymerisation,[4] a trialkoxy silane derivative for immobilisation on silica,[5] biotin for immobilisation onto a host protein (avidin or streptavidin)[6] or a phosphorus-containing moiety for immobilisation onto a host protein (lipase)[7] or alumina.[8] Whatever support is used, it must be pointed out that the anchoring functional group is introduced on the molecules subjected to immobilisation following a divergent synthesis. Indeed, the immobilisation strategy frequently needs two or more steps to install the anchoring functional group.[5b] A more direct strategy is therefore highly desirable, and only a few examples of this kind of convergent approach have been reported.[9]

Our goal is to propose a convergent approach for the immobilisation of ligands on the surface of metal oxide (e.g. alumina). To reach this goal, we proposed to use a methodology, developed by us[8a] and others,[8b], which is based on the reaction between a phosphonate group and an alumina surface to functionalise the surface with organic molecules. With this methodology, high loadings (up to 2 mmol/g) can be reached. The second aspect we would like to integrate into this strategy of immobilisation would be the possibility of spacing the anchoring group (phosphonate) from the molecule subjected to immobilisation by a linker of adjustable length and/or rigidity. Finally, since a convergent synthesis is highly desirable, we would like to functionalise the ligand with the phosphonate-terminated linker in only one step. To achieve the bond between the linker and the ligand, we have selected the Sonogashira cross-coupling, which is a well-documented[10] reaction and is tolerant towards a large number of functional groups. Furthermore, the choice of this cross-coupling is also motivated by the fact that many ligands used in homogeneous catalysis possess an aromatic ring (e.g. BINAP, phenanthroline and PYBOX) and interestingly, most of them are available with a halide atom (needed for the Sonogashira cross-coupling) on their aromatic ring. The goal of this work is summarised in Scheme 1. The ω-alkyne-phosphonate molecules **A** form the

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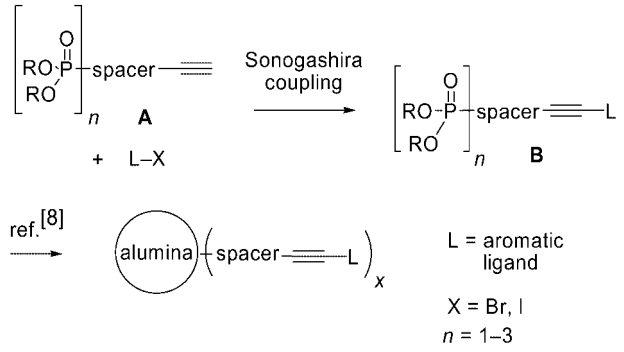
starting point of this strategy of immobilisation. The chemical nature of the spacer, selected for this study, is either an alkyl or ether chain.



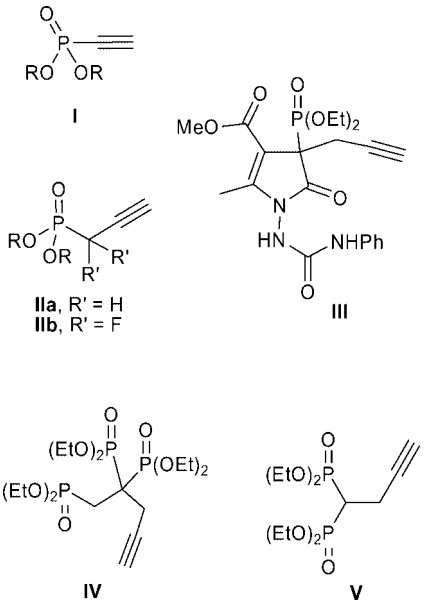

Scheme 1. Convergent strategy for the immobilisation of ligands on alumina.

In this paper, we report several routes for the synthesis of new ω-alkyne-mono-, di- and triphosphonates **A** and their use as substrates in Sonogashira cross-couplings to form molecules **B**. To illustrate the functionalisation of a ligand, 1,10-phenanthroline has been selected. It is worth mentioning that this strategy, proposed for the immobilisation of aromatic ligands used in homogeneous catalysis, can actually be applied to all kinds of aromatic molecules that would be useful for other applications (e.g. sensors and functionalised hybrids).

## Results and Discussion

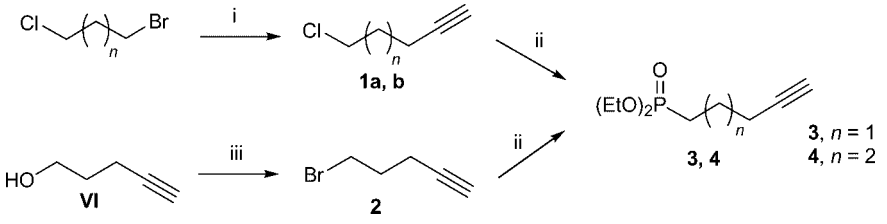
### Synthesis of ω-Alkyne-Phosphonates

To the best of our knowledge, only a few ω-alkyne-phosphonates have been reported in the literature (Scheme 2). Compound **I**,[11] has been submitted to the Sonogashira coupling, but very low yields have been reported.[12] This result is explained by the fact that compound **I** is actually an excellent Michael acceptor due to the existence of a conjugation between the phosphonate group and the triple bond. Among the compounds of type **II** (**IIa**[13] and **IIb**[14]), compound **IIa** is the easiest to synthesise. Unfortunately, its use in a Sonogashira cross-coupling is improbable because it mainly exists as its allenic form. The alkyne-phosphonate **III**, has been synthesised for its potential biological activities and has been engaged successfully in a Sonogashira cross–coupling,[15] thus illustrating the compatibility of this cross-coupling with the presence of a phosphonate group. Compound **IV** has been recently synthesised by our laboratory by the Michael addition of diethyl phosphite on vinylidene diphosphonate, followed by an alkylation step with propargyl bromide.[16] Finally, the synthesis of diphosphonate **V** has been reported, but only a few experimental details were mentioned.[17]




Scheme 2. Previously described alkynyl phosphonates.

The first goal of this work consisted of developing an efficient method to synthesise ω-alkyne-phosphonates containing an alkyl chain or ether chain. The two first ω-alkyne-phosphonates **3** and **4** possess an alkyl chain to separate the alkyne from the phosphonate. These compounds are obtained in a two-step procedure. The alkyne chlorides **1a** and **1b** were first synthesized according to a published method that involves the reaction of sodium acetylide in liquid ammonia with a chloro- or bromoalkyne[18] (Scheme 3). This step is actually tedious and must be carried out with care to avoid the contamination of the reaction media with acetone, which can come from the bottle of acetylene (acetone is the storage solvent). It is worth mentioning that compound **1a** is presently a commercial compound. The second step is an Arbuzov reaction,[19] engaging both the ω-chloroalkyne and triethylphosphite. Compounds **3** and **4** were isolated in moderate yields of 34% and 68%, respectively, after 3 days of heating (this reaction time is needed due to the low reactivity of the




Scheme 3. Synthesis of alkynyl phosphonates. i) HC≡CNa, liquid $NH_3$, –40 °C, 3 h, 78% ($n$ = 1), 57% ($n$ = 2). ii) $P(OEt)_3$, reflux, 3 d, 34% ($n$ = 1) **3**, 68% ($n$ = 2) **4**. iii) $PBr_3$ (0.33 equiv.), pyridine (cat.), diethyl ether, reflux, 2 h, 88%.

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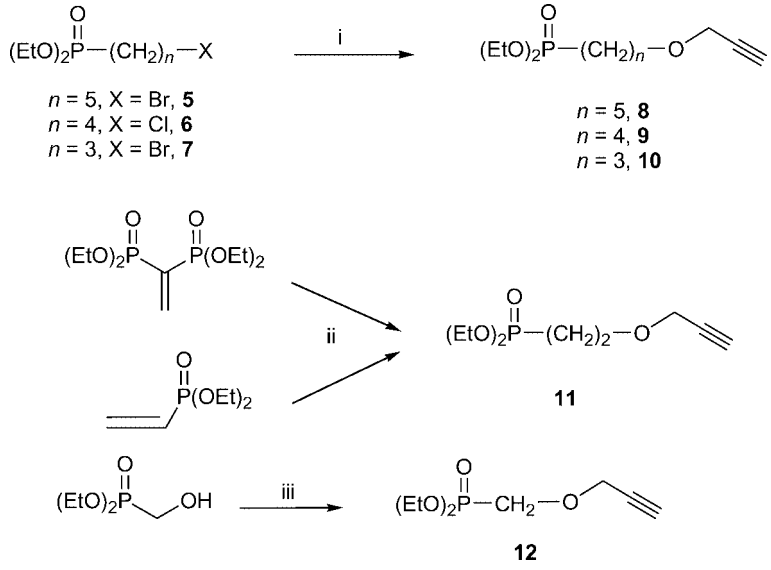
chloro group). The low yield obtained for compound **3** could be explained by the volatility of 5-choropentyne (**1a**). In order to reduce the reaction time, we attempted microwave activation[20] for these Arbuzov reactions, but unfortunately, after 15 min of heating, no conversion could be detected, and we did not investigate further. The Michaelis–Becker[21] reaction (the reaction between an alkyl halide and sodium diethylphosphite) represents an alternative way to introduce the phosphonate group. We attempted this reaction on the substrate **1a**, but a similar yield was obtained (34%). In order to improve the yield, we attempted another strategy starting from the commercially available ω-hydroxy-alkyne **VI**. The first step consists in a functional group transformation with phosphorus tribromide to get the ω-bromoalkyne **2**, which is heavier and less volatile than its chloride equivalent **1a**. Compound **2** was isolated a few times in good yield (80%) and fully characterised, but for no apparent reason, other attempts proved that this reaction was quite difficult to reproduce. Therefore, we finally preferred the first approach through a chloroalkyne.

The second family of ω-alkyne-phosphonates synthesised possesses an ether group to separate the phosphonate from the triple bond. To synthesise these molecules, we used propargyl alcohol or propargyl bromide (these are low-cost precursors, which are commercially available) as a source of the triple bond. It is worth noting that the presence of an ether group in the propargylic position (Scheme 4) is compatible with the Sonogashira cross-coupling.[22]

The diethyl (5-bromopentyl)phosphonate **5** was obtained in good yield by reacting an excess of dibromopentane with triethylphosphite under microwave irradiation.[20] This compound was submitted to a Williamson-type reaction with propargyl alcohol to produce compound **8** in 80% yield (Scheme 4). A similar strategy, with the shorter ω-halogeno-phosphonates as precursors, was applied for the synthesis of the ω-alkyne-phophonates **9** and **10**. The lower yields observed (78% and 70%, respectively) for the Williamson reactions are attributed either to the lower reactivity of the chloro derivative (to synthesise compound **9**) or the competition between the substitution and the elimination reaction, which is sensitive to the proximity of the phosphonate group (synthesis of compound **10**). A shorter ω-alkyne-phosphonate (compound **11**) was synthesised by the Michael addition of propargyl alcohol to diethyl vinylphosphonate in good yield (77%). The synthesis of a terminal diphosphonate on an identical carbon chain was attempted, but the loss of one of the diethylphosphonyl groups, according to a possible mechanism reported elsewhere,[16] produced the ω-alkyne-phosphonate **11**. Finally the shortest ω-alkyne-phosphonate **12**[23] was isolated in good yield (78%) in a two-step process, starting with the deprotonation of the diethyl hydroxymethylphosphonate at low temperature (–78 °C) with an excess of sodium hydride, followed by the addition of propargyl bromide at room temperature for 16 h.

Access to ω-alkyne-diphosphonates would also be of great use in estimating the benefit of the presence of two anchoring groups on the stability of the grafting onto alumina. Since our first attempt reported above failed, we looked at the alkylation of methylene diphosphonate **VII** with propargyl bromide.[17] This reaction leads to a mixture of compounds (mono- and dipropargyl) irrespective of the number of equiv. of propargyl bromide used. To avoid the formation of such a mixture of products, we used the vinylidene diphosphonate as a starting compound (Scheme 5). We first hydrogenated[24] this substrate and then deprotonated it with sodium hydride. We then alkylated it with propargyl bromide. For the deprotonation/alkylation step, we observed an effect of the temperature on the nature of the product formed. Indeed, if the deprotonation/alkylation




Scheme 4. Synthesis of alkynyl phosphonates with the alkyne in the propargylic position. i) 2 equiv. propargylic sodium alcoholate, DMF/THF, room temp., 16 h, 80% **8**, 16 h, 78% **9**, 72 h 70% **10**. ii) 1.5 equiv. propargylic sodium alcoholate, 0 °C, 3 h, 77%. iii) 1.6 equiv. NaH, THF, –78 °C, 30 min, 3 equiv. propargyl bromide, room temp., 16 h, 78%.

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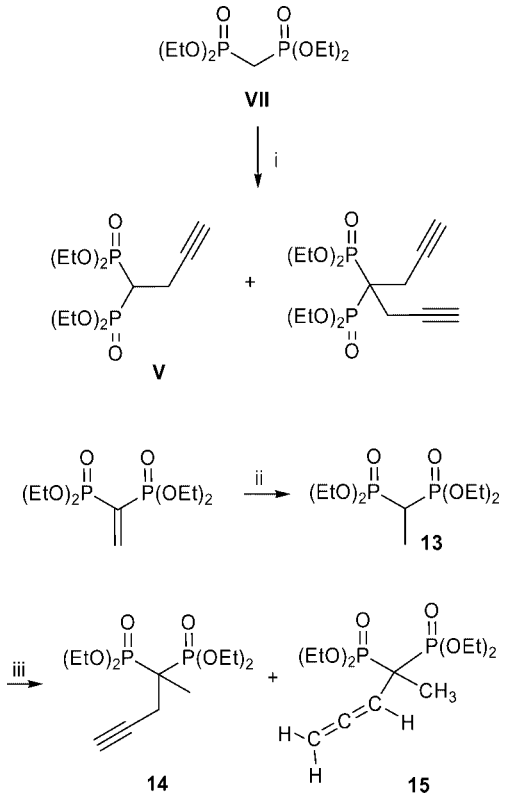
step is achieved at a temperature greater than 0 °C, a large amount (50% yield) of the allene derivative **15** is observed. At a temperature lower than 0 °C, no trace of allene **15** is detected in the crude product, and a good yield of compound **14** is obtained after distillation (90%).



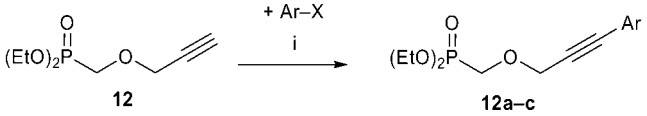

Scheme 5. Formation of alkynyl diphosphonate. i) 1.6 equiv. NaH, THF, –78 °C, 30 min, 3 equiv. propargyl bromide, room temp., 16 h. ii) $H_2$, Pd/C, 3 atm, ethanol, 3 h., room temp., 95%. iii) 1.6 equiv. NaH, THF, –78 °C, 30 min, 3 equiv. propargyl bromide, room temp., 16 h, 90%.

### Sonogashira Cross-Coupling Reaction

The Sonogashira cross-coupling reaction of a terminal acetylene with aryl or vinyl halides provides a powerful method for C($sp^2$)–C(sp) bond formation. The typical procedure for this coupling[25] uses a catalytic amount of palladium salt, a copper(I) complex (cocatalyst) and a base. A side product, resulting from the homocoupling reaction of the terminal alkyne (Glaser homocoupling[26]), is frequently observed, leading to increased difficulties associated with purification. Alkyne homocoupling results from the reaction of copper acetylide with an oxidative agent like dioxygen. Surprisingly, the presence of dioxygen does not always explain the Glaser homocoupling.[27] Recent work related to the Sonogashira cross-coupling demonstrates that the addition of copper salt as a cocatalyst can sometimes decrease the kinetics of the Sonogashira cross-coupling.[28] Furthermore, several copper-free Sonogashira cross-couplings have been published in recent years.[29]

Despite the number of copper-free methods, we first tested standard conditions with 4% of palladium complexes and 8% of copper salts in the presence of diisopropylamine as base. We tried different sources of palladium and applied the cross-coupling to 4-bromotoluene and 4-iodotoluene. For these reactions, we used an excess of phosphonoalkyne in an attempt to obtain a complete conversion of the aryl halide. Indeed, in these benchmark reactions, the aromatic halide mimics the aromatic ligand for which we expect to get a full conversion. The choice of solvent proved to be important as well. Indeed, a full conversion was obtained in acetonitrile, while a partial conversion (70% yield) was observed in THF. In both cases the following conditions

Table 1. Sonogashira cross-coupling with alkynyl phosphonate **12**.




i: **Method A**: $[PdCl_2(PPh_3)_2]$ (4 mol-%), CuI (8 mol-%), $iPr_2NH$ (4.7 equiv.) in $CH_3CN$ (30 mL). **Method B**: $[Pd_2dba_3]$ (1.5 mol-%), $PPh_3$ (6 mol-%), CuI (6 mol-%), $iPr_2NH$ (4.7 equiv.) in $CH_3CN$ (30 mL). **Method C**: $[PdCl_2(CH_3CN)_2]$ (2 mol-%), $HP(Cy)_3BF_4$ (8 mol-%), $Cs_2CO_3$ (1.6 equiv.) in $CH_3CN$ (10 mL)

| Entry | Ar–X | Method | Reaction temp. | Conversion of ArX [%][a] | Yield [%][b] | Product |
|---|---|---|---|---|---|---|
| 1 | 4-iodotoluene | A | room temp. | 100 | 94 | **12a** |
| 2 | | B | room temp. | 100 | 96 | |
| 3 | | C | 120 °C | 100 | 55 | |
| 4 | 4-bromotoluene | A | reflux | <5 | 0 | |
| 5 | | B | reflux | <5 | 0 | |
| 6 | | C | 120 °C | 100 | 74 | |
| 7 | 4-bromonitrobenzene | A | room temp. | 100 | 97 | **12b** |
| 8 | | B | room temp. | 100 | 96 | |
| 9 | | C | 120 °C | degradation | trace | |
| 10 | 4-bromopyridine | A | reflux | 75 | 59 | **12c**[c] |
| 11 | | B | reflux | 60 | 37 | |
| 12 | | C | 120 °C | 80 | 64 | |

[a] Conversion was determined by $^1H$ NMR spectroscopy. [b] Isolated yield. [c] Unstable product.

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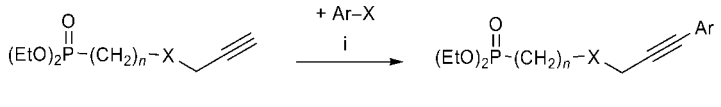
were used: phosphonoalkyne **12** (1.5 equiv.), $[PdCl_2(PPh_3)_2]$ (4 mol-%), copper iodide (8 mol-%) and diisopropylamine (4.7 equiv.) in acetonitrile at reflux.

As illustrated in Table 1, the reaction engaging an electron-deficient aryl bromide (Table 1, Entries 7 and 8) or an electron-rich iodide (Table 1, Entries 1 and 2) can be carried out at room temperature in the presence of copper iodide in very good yield. The $^1$H NMR spectra showed the presence of the homocoupling alkyne product (Glaser homocoupling), but the terminal alkyne was not present anymore. No improvement was observed with the use of $[PdCl_2(PPh_3)_2]$[22] or $[Pd_2dba_3]$[15] as the catalyst, which produce a large amount of the homocoupling side product. When unactivated aryl halides (Table 1, Entries 4, 5, 10 and 11) were used as substrates, this method was not efficient enough (poor conversions), and large amounts of homocoupling were obtained. A competition probably takes place between the cross-coupling and the homocoupling reactions.

In order to reduce the amount of the homocoupling product, a protocol without copper was tested.[28] After adaptation, the copper-free conditions employed $[PdCl_2(CH_3CN)_2]$ (2 mol-%), a tertiary phosphane generated in situ from $[HP(Cy)_3BF_4]$ (8 mol-%), a terminal alkyne (1.2 equiv.) and $Cs_2CO_3$ (1.6 equiv.) in acetonitrile at 120 °C in a sealed tube. These conditions typically provided selective transformation of the aryl halide to the cross-coupling product. As shown in Table 1, Entries 6 and 12, the method was efficient, and the coupling products were obtained in good yields. At the end of the reaction, the halide compound was fully consumed, and no trace of homocoupling side product was observed.

The best conditions found were applied to the Sonogashira cross-coupling of other ω-alkyne-monophosphonates (Table 2) and ω-alkyne-di- and triphosphonates (Table 3). As reported in these tables, both the conversions, determined by $^1$H NMR, and the yields were good. According to these results, the Sonogashira cross-coupling is not sensi-

Table 2. Sonogashira cross-coupling with alkynyl monophosphonate.




$n$ = 1, X = $CH_2$, **3**
$n$ = 2, X = O, **11**
$n$ = 5, X = O, **8**

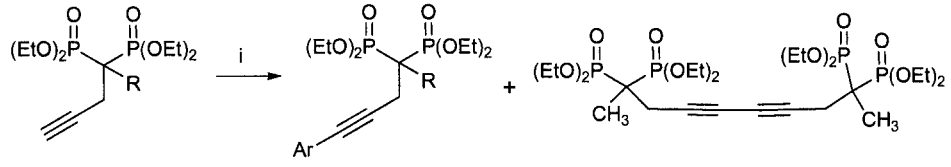
$n$ = 1, **3a–b**
$n$ = 2, **11a–c**
$n$ = 5, **8 a–b**

i: **Method A**: $[PdCl_2(PPh_3)_2]$ (4 mol-%), CuI (8 mol-%), $i$Pr$_2$NH (4.7 equiv.) in $CH_3CN$ (30 mL). **Method C**: $[PdCl_2(CH_3CN)_2]$ (2 mol-%), $HP(Cy)_3BF_4$ (8 mol-%), $Cs_2CO_3$ (1.6 equiv.) in $CH_3CN$ (10 mL)

| Entry | Alkyne | Ar–X | Method | Reaction temp. | Conversion of ArX [%][a] | Yield [%][b] | Product |
|---|---|---|---|---|---|---|---|
| 1 | **3** | 4-iodotoluene | A | room temp. | 100 | 56 | **3a** |
| 2 | **3** | 4-bromonitrobenzene | A | reflux | 100 | 53 | **3b** |
| 3 | **11** | 4-iodotoluene | A | room temp. | 100 | 97 | **11a** |
| 4 | **11** | 4-bromotoluene | C | 120 °C | 95 | 60 | **11a** |
| 5 | **11** | 4-bromonitrobenzene | A | room temp. | 100 | 90 | **11b** |
| 6 | **11** | 4-bromopyridine | C | 120 °C | 100 | 90 | **11c** |
| 7 | **8** | 4-iodotoluene | A | room temp. | 100 | 95 | **8a** |
| 8 | **8** | 4-bromonitrobenzene | A | room temp. | 100 | 91 | **8b** |

[a] Conversion was determined by $^1$H NMR spectroscopy. [b] Isolated yield.

Table 3. Sonogashira cross-coupling with alkynyl di- or triphosphonates.




R = Me, **14**
R = $CH_2PO(OEt)_2$, **IV**

R = Me, **14a-b**
R = $CH_2PO(OEt)_2$, **16a-b**

**14d** (Entry 2)

i: **Method A**: $[PdCl_2(PPh_3)_2]$ (4 mol-%), CuI (8 mol-%), $i$Pr$_2$NH (4.7 equiv.) in $CH_3CN$ (30 mL)

| Entry | Alkyne | Ar–X | Reaction temp. | Conversion of ArX [%][a] | Yield [%][b] | Product |
|---|---|---|---|---|---|---|
| 1 | **14** | 4-iodotoluene | room temp. | 100 | 90 | **14a** |
| 2 | **14** | 4-bromonitrobenzene | reflux | 100 | 91 | **14b** |
| 3 | **IV** | 4-iodotoluene | room temp. | 100 | 77 | **16a** |
| 4 | **IV** | 4-bromonitrobenzene | reflux | 100 | 96 | **16b** |

[a] Conversion was determined by $^1$H NMR spectroscopy. [b] Isolated yield.

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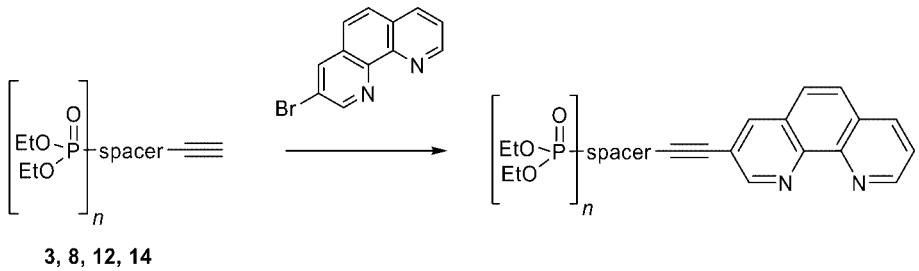
Table 4. Sonogashira cross-coupling with an aryl halide and alkynyl phosphonates.




**3, 8, 12, 14**

*n* = 1-3

**Method B**: [$Pd_2dba_3$] (1.5 mol-%), $PPh_3$ (6 mol-%), CuI (6 mol-%), $iPr_2NH$ (4.7 equiv.) in $CH_3CN$ (30 mL). **Method C**: [$PdCl_2(CH_3CN)_2$] (2 mol-%), $HP(Cy)_3BF_4$ (8 mol-%), $Cs_2CO_3$ (1.6 equiv.) in $CH_3CN$ (10 mL)

| Entry | Alkyne | Method | Reaction temp. | Conversion of ArX [%][a] | Yield [%][b] | Product |
|---|---|---|---|---|---|---|
| 1 | **12** | B | reflux | 100 | 78 | **12d** |
| 2 | **8** | B | reflux | 100 | 74 | **8c** |
| 3 | **8** | C | 120 °C | 100 | 82 | **8c** |
| 4 | **3** | B | reflux | 100 | 92 | **3c** |
| 5 | **14** | B | reflux | 100 | 80 | **14c** |
| 6 | **IV** | B | reflux | 0 | 0 | – |

[a] Conversion was determined by $^1H$ NMR spectroscopy. [b] Isolated yield.

tive to the spacer length between the alkyne and the phosphonate group. Furthermore, the presence of multiple phosphonate group led to the Sonogashira cross-coupling products in good yield. In only one case (Table 3, Entry 2), did we observe the presence of the homocoupling side product **14d**.

Finally the cross-coupling conditions were applied to an aromatic ligand. 1,10-phenanthroline, which is readily available with a bromine atom in position 3,[30] was chosen. This choice results from both its chemical stability (to dioxygen and water) and its value in metallo-catalysis.[31] The chemical stability is strongly desired for applications in both homogeneous and heterogeneous catalysis. 3-bromo-1,10-phenanthroline was subjected to Sonogashira cross-coupling engaging different ω-alkyne-phosphonates. The isolated yields were good, as depicted in Table 4, except for the coupling of the triphosphonate **IV**. For the cross-coupling engaging the alkyne-diphosphonate **14**, a trace of the homocoupling side product **14d** was isolated and fully characterised. It is worth mentioning that the purification step for each reaction engaging 1,10-phenanthroline was slightly different. Indeed, a washing step with potassium cyanide was added in order to eliminate the metallic salts complexed with the product.

## Conclusions

Efficient syntheses of new ω-alkyne-mono- and diphosphonates are reported. A very convenient access to ω-alkyne-phosphonates employs either a propargyl alcohol or propargyl bromide as the source of the alkyne part. According to this approach, several ω-alkyne diphosphonates have been easily prepared on large scale. The second step of the present work consisted of performing the Sonogashira cross-coupling between the alkyne-phosphonate and aromatic halide. The yields are usually good to very good. Nevertheless, on a few occasions, the homocoupling of the alkyne is detected. In such cases, the use of copper-free conditions for the Sonogashira coupling avoids the formation of this side product. We finally applied these Sonogashira cross-coupling conditions to 3-bromo-1,10-phenanthroline as an illustration of the functionalisation of an aromatic ligand exhibiting interest for both homogeneous and heterogeneous metallo-catalysis.

The two first steps of a general convergent strategy for immobilising ligands on an inorganic support is reported. The ultimate immobilisation of ligands onto alumina will be reported in the near future. It must be pointed out that the new alkyne-phosphonates could also have great potential to perform the Huisgen reaction ("click chemistry"), which has received considerable attention in the last few years.[32,33]

## Experimental Section

**General:** Most of the reactions were carried out under a nitrogen or argon atmosphere with magnetic stirring and monitored by TLC with silica plates. Synthesized products were purified by distillation or flash column chromatography on silica gel. IR spectra of solids or neat liquids were obtained with a Fourier-transform Perkin–Elmer Spectrum One spectrometer with an ATR accessory. Only significant absorptions are listed. The $^1H$, $^{31}P$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$, with a Bruker AC 250 or a Bruker AC 400 spectrometer. The chemical shifts ($\delta$) are expressed in ppm, and conventional abbreviations are used. Mass spectra were recorded with a QTOF Micro (Waters) spectrometer with electrospray ionisation (ESI, positive mode), lockspray PEG, infusion introduction

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at 5 mL/min, a source temperature of 80 °C and a desolvation temperature of 120 °C. Elemental analyses were performed with an automatic CHNS-O ThermoQuest apparatus.

Alkyne chlorides **1a** and **1b** were synthesised according to the literature procedures.[34] 5-Bromopentyne (**2**),[35] diethyl (bromopropyl)phosphonate (**6**)[36] and diethyl (chlorobutyl)phosphonate (**7**),[37] were prepared according to the literature procedures. Diethyl (5-bromopentyl)phosphonate (**5**) was synthesised by a method previously reported by our laboratory.[20] Tetraethyl ethylidenebis(phosphonate),[38] diethyl vinylphosphonate,[39] hexaethyl (pent-4-ynyl)-1,2,2-trisphosphonate (**IV**),[16] diethyl (hydroxymethyl)phosphonate[40] and tetraethyl ethyl-1,1-bis(phosphonate) (**13**),[24] were synthesised according to reported procedures.

**Diethyl (Pent-4-ynyl)phosphonate (3):** In a dry 50-mL round-bottomed flask, placed under argon and fitted with a condenser and a Dean–Stark trap, were placed 5-chloropentyne (**1a**) (2.0 g, 19.5 mmol) and triethyl phosphite (5.4 g, 31.2 mmol). The reaction mixture was heated at reflux for 80 h. The product was purified by kugelrohr distillation (50–60 °C/10 mTorr) to yield compound **3** (1.1 g, 34% yield) as a colourless oil. IR (neat): $\tilde{\nu}$ = 3294 (C≡C–H), 2114 (C≡C), 1227 (P=O), 1023, 955 (P–O) cm$^{-1}$. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.33 (t, $^3J$ = 7 Hz, 6 H, 2 × C$H_3$), 1.75–1.95 [m, 4 H, (C$H_2$)$_2$PO], 1.99 (t, $^4J$ = 3 Hz, 1 H, C≡C$H$), 2.30 [dt, $^4J$ = 3 Hz, $^3J$ = 7 Hz, 2 H, C$H_2$(CH$_2$)$_2$PO], 4.10 (dq, $^3J$ = 7 Hz, $^3J$ = 7 Hz, 4 H, CH$_3$C$H_2$O) ppm. $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = 32.30 ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.7 (d, $^3J$ = 6 Hz, $C$H$_3$CH$_2$O), 19.5 (d, $^2J$ = 18 Hz, $C$H$_2$CH$_2$PO), 21.9 [d, $^3J$ = 5 Hz, $C$H$_2$(CH$_2$)$_2$PO], 24.9 (d, $^1J$ = 142 Hz, $C$H$_2$PO), 61.9 (d, $^2J$ = 7 Hz, CH$_3C$H$_2$OP), 69.8 (s, C≡$C$H), 83.3 (s, $C$≡CH) ppm. MS (11 eV): *m*/*z* (%) = 205 (26) [M + H]$^+$, 176 (22), 165 (18), 148 (100), 125 (65), 109 (37), 97 (57), 84 (34), 65 (33). HRMS (ES-TOF): calcd. for $C_9H_{18}O_3P$ [M + H]$^+$ 205.0994; found 205.0992.

**Diethyl (Hex-5-ynyl)phosphonate (4):** In a dry 50-mL round-bottomed flask, placed under argon and fitted with a condenser and a Dean Stark trap, were placed 6-chlorohexyne (**1b**) (4.5 g, 38.6 mmol) and triethyl phosphite (10.6 g, 61.8 mmol). The reaction mixture was heated at reflux for 80 h. The product was purified by kugelrohr distillation (125 °C/10 mTorr) to give alkyne **4** (5.7 g, 68% yield) as a colourless oil. IR (neat): $\tilde{\nu}$ = 3295 (C≡C–H), 2116 (C≡C), 1223 (P=O), 1017, 960 (P–O) cm$^{-1}$. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.33 (t, $^3J$ = 7 Hz, 6 H, 2 × C$H_3$), 1.55–1.85 [m, 6 H, (C$H_2$)$_3$PO], 1.95 (t, $^4J$ = 3 Hz, 1 H, C≡C$H$), 2.21 [dt, $^4J$ = 3 Hz, $^3J$ = 7 Hz, 2 H, C$H_2$(CH$_2$)$_3$PO], 4.10 (dq, $^3J$ = 7 Hz, $^3J$ = 7 Hz, 4 H, CH$_3$C$H_2$O) ppm. $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = 32.80 ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, $C$H$_3$CH$_2$O), 18.3 [d, $^4J$ = 1 Hz, $C$H$_2$(CH$_2$)$_3$PO], 21.9 [d, $^3J$ = 5 Hz, $C$H$_2$(CH$_2$)$_2$PO], 25.6 (d, $^1J$ = 141 Hz, $C$H$_2$PO), 29.4 (d, $^2J$ = 17 Hz, $C$H$_2$CH$_2$PO), 61.8 (d, $^2J$ = 7 Hz, CH$_3C$H$_2$O), 69.1 (s, C≡$C$H), 84.1 (s, $C$≡CH) ppm. MS (8 eV): *m*/*z* (%) = 219 (24) [M + H]$^+$, 179 (61), 162 (20), 152 (72), 138 (18), 125 (100), 108 (41), 97 (57), 81 (57), 65 (23). HRMS (ES-TOF): calcd. for $C_{10}H_{19}O_3PNa$ [M+Na]$^+$ 241.0970; found 241.0963.

**Diethyl [5-(Prop-2-ynyloxy)pentyl]phosphonate (8):** In a dry 50-mL round-bottomed flask, placed under nitrogen, freshly distilled THF (20 mL) was added to sodium hydride (1.2 g, 60% in oil, 34.8 mmol), which had been previously washed with pentane (3 × 10 mL). The solution was cooled to –78 °C. A solution of propargylic alcohol (1.3 g, 23.2 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 30 min at –78 °C. A solution of diethyl (5-bromopentyl)phosphonate (3.3 g, 11.5 mmol) in DMF (20 mL) was then added. The solution was stirred for 16 h, and the reaction temperature was warmed slowly to room temperature. The solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (15 mL). The solution was extracted with dichloromethane (3 × 25 mL). The organic phase was dried with $MgSO_4$, filtered, concentrated, and the crude product was purified by kugelrohr distillation (110 °C/10 mTorr) to produce compound **8** (2.38 g, 79% yield) as a colourless oil. IR (neat): $\tilde{\nu}$ = 3280 (C≡C–H), 2118 (C≡C), 1223 (P=O), 1098 (C–O), 1020, 957 (P–O) cm$^{-1}$. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.32 (t, $^3J$ = 7 Hz, 6 H, 2 × C$H_3$), 1.50–2.00 (m, 8 H, $CH_2CH_2CH_2CH_2$), 2.42 (t, $^4J$ = 3 Hz, 1 H, C$H$), 3.51 (t, $^3J$ = 6 Hz, 2 H, C$H_2$O), 4.09 (m, 6 H, 2 × C$H_2$OP, $CH_2$C≡C) ppm. $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = 33.67 ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.4 (d, $^3J$ = 6 Hz, 2 × $C$H$_3$), 21.6 [d, $^3J$ = 5 Hz, $C$H$_2$(CH$_2$)$_2$PO], 25.5 (d, $^1J$ = 157 Hz, $C$H$_2$PO), 27.1 (d, $^2J$ = 17 Hz, $C$H$_2$CH$_2$PO), 29.9 (s, $C$H$_2$CH$_2$O), 58.0 (s, $C$H$_2$C≡C), 61.3 (d, $^2J$ = 5 Hz, 2 × $C$H$_2$OP), 69.9 (s, $C$H$_2$O), 74.1 (s, C≡$C$H), 79.9 (s, $C$≡CH) ppm. MS (12 eV): *m*/*z* (%) = 263 (38) [M]$^+$, 223 (100), 207 (20), 179 (34), 177 (56), 165 (62), 152 (57), 151 (65), 138 (24), 137 (63), 125 (99), 109 (42). HRMS (ES-TOF): calcd. for $C_{12}H_{24}O_4P$ [M + H]$^+$ 264.1412; found 263.1426.

**Diethyl [4-(Prop-2-ynyloxy)butyl]phosphonate (9):** In a dry 50-mL round-bottomed flask, placed under nitrogen, freshly distilled THF (20 mL) was added to sodium hydride (340 mg, 60% in oil, 12.0 mmol), which had been previously washed with pentane (3 × 10 mL). The solution was cooled to –78 °C. A solution of propargylic alcohol (504 mg, 9.0 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 30 min at –78 °C. A solution of diethyl (4-chlorobutyl)phosphonate (1.0 g, 3.0 mmol) in DMF (20 mL) was then added. The solution was stirred for 16 h, and the reaction temperature was warmed slowly to room temperature. The solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (15 mL). The solution was extracted with dichloromethane (3 × 25 mL). The organic phase was dried with $MgSO_4$, filtered, concentrated, and the crude product was purified by kugelrohr distillation (105 °C/10 mTorr) to produce compound **9** (580 mg, 78% yield) as a colourless oil. IR (neat): $\tilde{\nu}$ = 3290 (C≡C-H), 2111 (C≡C), 1237 (P=O), 1099 (C-O), 1022, 956 (P-O) cm$^{-1}$. $^1$H NMR (250 MHz, $CDCl_3$): $\delta$ = 1.07 (t, $^3J$ = 7 Hz, 6 H,C$H_3$CH$_2$O), 1.36–1.55 (m, 6 H, C$H_2C H_2C H_2$P), 2.20 (t, $^4J$ = 2 Hz, 1 H, C≡C$H$), 3.25 (t, $^3J$ = 7 Hz, 2 H, C$H_2$O), 3.85–4.05 (m, 6 H, 2 × CH$_3$C$H_2$O, OC$H_2$C≡CH) ppm. $^{31}$P NMR (101.25 MHz, $CDCl_3$): $\delta$ = 32.19 ppm. $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, 2 × $C$H$_3$CH$_2$O), 19.7 (d, $^2J$ = 5 Hz, $C$H$_2$CH$_2$PO), 25.7 (d, $^1J$ = 141 Hz, $C$H$_2$PO), 30.6 (d, $^3J$ = 17 Hz, $C$H$_2$CH$_2$CH$_2$PO), 58.4 (s, $C$H$_2$C≡C), 61.8 (d, $^2J$ = 5 Hz, CH$_3C$H$_2$O), 69.6 (s, $C$H$_2$OCH$_2$C≡C), 74.6 (s, CH$_2$C≡$C$H), 80.2 (s, CH$_2C$≡CH) ppm. MS (12 eV): *m*/*z* (%) = 229 (52) [M + H]$^+$, 228 (1) [M]$^+$, 193 (100), 165 (55), 137 (74), 111 (21). HRMS (ES-TOF): calcd. for $C_{11}H_{22}O_4P$ [M + H]$^+$ 249.1256; found 249.1255.

**Diethyl [3-(Prop-2-ynyloxy)propyl]phosphonate (10):** In a dry 50-mL round-bottomed flask, placed under nitrogen, freshly distilled THF (20 mL) was added to sodium hydride (500 mg, 60% in oil, 12.9 mmol), which had been previously washed with pentane (3 × 10 mL). The solution was cooled to –78 °C. A solution of propargylic alcohol (550 mg, 9.7 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 30 min at –78 °C. A solution of diethyl (3-bromopropyl)phosphonate (1.0 g, 3.2 mmol) in DMF (20 mL) was then added. The solution was stirred for 16 h, and the reaction temperature was warmed slowly to room temperature. The solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (15 mL). The solution was extracted with dichloromethane (3 × 25 mL). The organic phase was dried with $MgSO_4$, filtered, concentrated, and the crude product was purified by chromatography on silica gel (ethyl acetate) to give

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compound **10** (530 mg, 70% yield) as a colourless oil. IR (neat): $\tilde{\nu}$ = 3280 (C≡C–H), 2112 (C≡C), 1237 (P=O), 1099 (C–O), 1020, 955 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.18 (t, $^3J$ = 7 Hz, 6 H, C$H_3$CH$_2$O), 1.45–1.80 (m, 4 H, C$H_2$C$H_2$P), 2.29 (t, $^4J$ = 2 Hz, 1 H, C≡C$H$), 3.42 (t, $^3J$ = 7 Hz, 2 H, C$H_2$O), 3.85–4.05 (m, 6 H, 2 × CH$_3$C$H_2$O, OC$H_2$C≡CH) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 32.99 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.4 (d, $^3J$ = 6 Hz, 2 × $C$H$_3$CH$_2$O), 22.3 (d, $^1J$ = 142 Hz, $C$H$_2$PO), 22.7 (d, $^2J$ = 5 Hz, $C$H$_2$CH$_2$PO), 58.1 (s, $C$H$_2$C≡C), 61.5 (d, $^2J$ = 5 Hz, CH$_3$$C$H$_2$O), 69.9 (s, $C$H$_2$OCH$_2$C≡C), 74.3 (s, CH$_2$C≡$C$H), 79.6 (s, CH$_2$$C$≡CH) ppm. MS (12 eV): *m*/*z* (%) = 259 (44) [M + H]$^+$, 258 (1) [M]$^+$, 179 (100), 152 (39), 151 (31), 125 (55), 123 (51), 105 (22). HRMS (ES-TOF): calcd. for $C_{10}H_{19}O_4PNa$ [M + Na]$^+$ 257.0919; found 257.0930.

**Diethyl [2-(Prop-2-ynyloxy)ethyl]phosphonate (11):** In a dry 50-mL round-bottomed flask, placed under nitrogen, freshly distilled THF (15 mL) was added to sodium hydride (2.6 g, 60% in oil, 74.7 mmol), which had been previously washed with pentane (3 × 10 mL). The solution was cooled to –78 °C. A solution of propargylic alcohol (2.8 g, 50.0 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 30 min at –78 °C. A solution of diethyl vinylphosphonate (2.7 g, 16.6 mmol) or tetraethyl vinylidenediphosphonate (5.0 g, 16.6 mmol) in THF (5 mL) was then added. The solution was stirred for 2 h, and the reaction temperature was warmed slowly to room temperature. The solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (25 mL). The solution was extracted with dichloromethane (3 × 25 mL). The organic phase was dried with $MgSO_4$, filtered, concentrated, and the crude product was purified by kugelrohr distillation (100 °C/10 mTorr) to produce compound **11** (77% yield) as a colourless oil. IR: $\tilde{\nu}$ = 3293 (C≡C–H), 2112 (C≡C), 1224 (P=O), 1096 (C–O), 1022, 957 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.33 (t, $^3J$ = 7 Hz, 6 H, 2 × C$H_3$), 2.13 (dt, $^2J$ = 26 Hz, $^3J_{HH}$ = 7 Hz, 2 H, PC$H_2$), 2.43 (t, $^4J$ = 3 Hz, 1 H, C≡C$H$), 3.77 (dt, $^3J$ = 12 Hz, 2 H, C$H_2$O), 4.11 (m, 4 H, 2 × CH$_3$C$H_2$O), 4.17 (d, $^4J$ = 2 Hz, 2 H, OC$H_2$C≡C) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 29.80 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.7 (d, $^3J$ = 6 Hz, 3 × $C$H$_3$), 27.2 (d, $^1J$ = 140 Hz, P$C$H$_2$), 58.4 (s, O$C$H$_2$), 62.1 (d, $^3J$ = 6 Hz, 2 × PO$C$H$_2$), 64.2 (s, O$C$H$_2$), 75.1 (s, C≡$C$H), 79.6 (s, $C$≡CH) ppm. MS (12 eV): *m*/*z* (%) = 221 (42) [M + H]$^+$, 181 (58), 153 (54), 125 (100), 111 (31). $C_9H_{17}O_4P$ (220.20): calcd. C 49.09, H 7.78; found C 48.92, H 8.36. HRMS (ES-TOF): calcd. for $C_9H_{18}O_4P$ [M + H]$^+$ 221.0943; found 221.0934.

**Diethyl [(Prop-2-ynyloxy)methyl]phosphonate (12):** In a dry 100-mL round-bottomed flask, placed under nitrogen, freshly distilled THF (30 mL) was added to sodium hydride (2.1 g, 60% in oil, 52.5 mmol), which had been previously washed with pentane (3 × 10 mL). The solution was cooled to –78 °C. A solution of diethyl (hydroxymethyl)phosphonate (6.0 g, 35.0 mmol) in THF (10 mL) was added dropwise. The solution was stirred for 90 min at –78 °C. A solution of propargyl bromide (12.7 g, 107 mmol) in THF (10 mL) was then added. The solution was stirred for 12 h, and the reaction temperature was warmed slowly to room temperature. The solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (25 mL). The solution was extracted with dichloromethane (3 × 25 mL). The organic phase was dried with $MgSO_4$, filtered, concentrated, and the crude product was purified by kugelrohr distillation (90 °C/10 mTorr) to produce compound **12** (78% yield) as a colourless oil. IR (neat): $\tilde{\nu}$ = 3281 (C≡C–H), 2114 (C≡C), 1223 (P=O), 1099 (C–O), 1026, 960 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.36 (t, $^3J$ = 7 Hz, 6 H,C$H_3$CH$_2$O), 2.50 (t, $^4J$ = 9 Hz, 1 H, C≡C$H$), 3.88 (d, $^2J$ = 10 Hz, 2 H, PC$H_2$O), 4.19 (m, 4 H, CH$_3$C$H_2$O), 4.29 (d, $^2J_{PH}$ = 2 Hz, 2 H, OC$H_2$C≡CH) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 21.80 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.4 (d, $^3J$ = 6 Hz, $C$H$_3$CH$_2$O), 60.0 (d, $^2J$ = 9 Hz, CH$_3$$C$H$_2$OP), 62.9 (d, $^3J$ = 4 Hz, O$C$H$_2$C≡CH), 63.3 (d, $^1J$ = 104 Hz, P$C$H$_2$O), 75.8 (s, C≡$C$H), 78.3 (s, $C$≡CH) ppm. MS (12 eV): *m*/*z* (%) = 207 (33) [M + H]$^+$, 152 (19), 125 (100), 108 (24), 97 (47). $C_8H_{15}O_4P$ (206.18): calcd. C 46.60, H 7.33; found C 46.98, H 7.70. HRMS (ES-TOF): calcd. for $C_8H_{16}O_4P$ [M + H]$^+$ 207.0786; found 207.0785.

**Tetraethyl [(Methylprop-2-ynyl)methylene]diphosphonate (14):** In a dry 50-mL round-bottomed flask, placed under nitrogen, freshly distilled THF (10 mL) was added to sodium hydride (170 mg, 60% in oil, 5.0 mmol), which had been previously washed with pentane (3 × 5 mL). The solution was cooled to –78 °C. A solution of tetraethyl ethyl-1,1-diphosphonate (**13**, 1.0 g, 3.3 mmol) in THF (5 mL) was added dropwise. The solution was stirred for 30 min at –78 °C. A solution of propargyl bromide (1.2 g, 9.9 mmol) in THF (5 mL) was then added. The solution was stirred for 16 h at –78 °C, and the reaction temperature was warmed slowly to room temperature. The solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (15 mL). The solution was extracted with dichloromethane (3 × 20 mL). The organic phase was dried with $MgSO_4$, filtered, concentrated, and the crude product was purified by kugelrohr distillation (135 °C/10 mTorr) to produce alkyne **14** (90% yield) as a colourless oil. IR (neat): $\tilde{\nu}$ = 3281 (C≡C–H), 2114 (C≡C), 1233 (P=O), 1016, 959 (P–0) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.35 (t, $^3J$ = 7 Hz, 12 H, 4 × C$H_3$CH$_2$O), 1.57 (t, $^3J$ = 16 Hz, 3 H, C$H_3$), 2.07 (t, $^4J$ = 3 Hz, 1 H, C≡C$H$), 2.84 (tt, $^3J$ = 3 Hz, $^2J$ = 15 Hz, 2 H, C$H_2$C≡C), 4.20 (m, 8 H, 4 × CH$_3$C$H_2$O) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 25.40 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.7 (m, 5 × $C$H$_3$), 23.3 (t, $^3J$ = 3 Hz, C$H_2$C≡C), 40.0 (t, $^1J$ = 134 Hz, P$C$P), 63.2 (d, $^3J$ = 6 Hz, 4 × PO$C$H$_2$), 71.7 (s, C≡$C$H), 79.4 (t, $^3J$ = 10 Hz, $C$≡CH) ppm. MS (18 eV): *m*/*z* (%) = 341 (13) [M + H]$^+$, 313 (31), 285 (51), 257 (65), 229 (100), 175 (16), 147 (17). HRMS (ES-TOF): calcd. for $C_{13}H_{27}O_6P_2$ [M + H]$^+$ 341.1283; found 341.1287.

**Tetraethyl [Methyl(buta-1,2-dienyl)methylene]diphosphonate (15):** IR (neat): $\tilde{\nu}$ = 1234 (P=O), 1018, 954 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.33 (t, $^3J$ = 7 Hz, 12 H, 4 × C$H_3$CH$_2$O), 1.50 (t, $^3J$ = 16 Hz, 3 H, C$H_3$), 4.17 (m, 8 H, 4 × CH$_3$C$H_2$O), 4.98 (dt, $J$ = 6 Hz, $J$ = 10 Hz, 2 H, =CH$_2$), 5.59 (quint, $J$ = 6 Hz, 1 H, CH) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 22.97 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 15.5 (t, $^3J$ = 6 Hz, $C$H$_3$), 16.4 (m, 4 × $C$H$_3$), 41.1 (t, $^1J$ = 134 Hz, P$C$P), 63.6 (m, 4 × PO$C$H$_2$), 79.1 (t, $^5J$ = 3 Hz, C=$C$H$_2$), 88.35 (t, $^3J$ = 12 Hz, $C$H=C), 209.5 (t, $^4J$ = 10 Hz, $C$=CH$_2$) ppm. MS (14 eV): *m*/*z* (%) = 340 (21) [M]$^+$, 312 (23), 284 (53), 256 (68), 228 (100), 203 (52), 163 (39), 147 (31), 129 (25), 99 (37), 81 (24), 65 (41). HRMS (ES-TOF): calcd. for $C_{13}H_{27}O_6P_2$ [M + H]$^+$ 341.1283; found 341.1289.

**General Procedure for the Sonogashira Coupling with CuI**

**Method A:** In a dry 50-mL round-bottomed flask, placed under argon and fitted with a reflux condenser, were placed aryl halide (0.6 mmol), [$PdCl_2(PPh_3)_2$] (17 mg, 4 mol-%) and copper iodide (9 mg, 8 mol-%) in freshly distilled $CH_3CN$ (30 mL). A solution of alkyne (0.92 mmol) in diisopropylamine (0.4 mL) was added. The reaction mixture was heated at reflux for 12 h. After cooling the mixture to room temperature, the solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (15 mL). The solution was extracted with dichloromethane (3 × 15 mL). The organic phase was dried with $MgSO_4$, filtered,

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concentrated, and the crude product was purified by kugelrohr distillation or by chromatography on silica gel.

**Method B:** In a dry 50-mL round-bottomed flask, placed under argon and fitted with a reflux condenser, were placed aryl halide (0.6 mmol), tris(benzylideneacetone)dipalladium {[$Pd_2(dba)_3$], 8 mg, 1.5 mol-%}, triphenylphosphane (9 mg, 6 mol-%) and copper iodide (7 mg, 6 mol-%) in freshly distilled $CH_3CN$ (30 mL). A solution of alkyne (0.92 mmol) in diisopropylamine (0.4 mL) was added. The reaction mixture was heated at reflux for 12 h. After cooling the mixture to room temperature, the solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (15 mL). The solution was extracted with dichloromethane (3 × 15 mL). The organic phase was dried with $MgSO_4$, filtered, concentrated, and the crude product was purified by kugelrohr distillation or by chromatography on silica gel.

**Method C. General Procedure for the Sonogashira Coupling without CuI:** In a dry 20-mL tube, placed under argon, were placed alkyl halide (0.6 mmol), dichloro bis(acetonitrile)palladium(II) {[$PdCl_2(CH_3CN)_2$], 3 mg, 2 mol-%}, tri(cyclohexyl)phosphonium tetrafluoroborate (18 mg, 8 mol-%) and cesium carbonate (313 mg, 0.96 mmol) in freshly distilled $CH_3CN$ (10 mL). The slightly yellow suspension was stirred for 20 min. Then a solution of alkyne (0.72 mmol) in $CH_3CN$ (3 mL) was added. The tube was sealed with a Teflon® valve, and the reaction mixture was heated at 120 °C for 12 h. The resulting suspension was allowed to reach room temperature, the solution was evaporated to dryness in vacuo, and saturated aqueous ammonium chloride was added (15 mL). The solution was extracted with dichloromethane (3 × 15 mL). The organic phase was dried with $MgSO_4$, filtered, concentrated, and the crude product was purified by kugelrohr distillation or by chromatography on silica gel.

**Diethyl [5-(*p*-Tolyl)pent-4-ynyl]phosphonate (3a):** Method A was employed with 4-iodotoluene (130 mg, 0.6 mmol) and alkyne **3** (202 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 90:10). Yield: 95 mg (56%) of a colourless oil. IR (neat): $\tilde{\nu}$ = 1231 (P=O), 1097 (C–O), 1023, 955 (P–0), 816 $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.28 (t, $^3J$ = 7 Hz, 6 H, C$H_3$CH$_2$O), 1.77–1.95 [m, 4 H, (C$H_2$)$_2$PO], 2.46 (dt, $^4J$ = 3 Hz, $^3J$ = 6 Hz, 2 H, C$H_2$C≡C), 3.90–4.10 (m, 4 H, C$H_3$CH$_2$O), 7.02 (d, $^3J$ = 7 Hz, 2 × C$H$CCH$_3$), 7.21 (d, $^3J$ = 7 Hz, 2 × C$H$CC≡C) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 32.70 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, $C$H$_3$CH$_2$O), 20.6 (d, $^2J$ = 18 Hz, $C$H$_2$CH$_2$PO), 21.7 (s, CH$_3$Ar), 22.3 (d, $^3J$ = 4 Hz, $C$H$_2$C≡CH), 25.1 (d, $^1J$ = 142 Hz, $C$H$_2$PO), 62.0 (d, $^2J$ = 6 Hz, CH$_3C$H$_2$O), 82.1 (s, C≡$C$C$_{arom}$), 88.1 (s, $C$≡CC$_{arom}$), 120.9 (s, 2 × $C$C≡C), 129.4 (s, 2 × $C$HCCH$_3$), 132.4 (s, $C$HCC≡C), 138.1 (s, $C$CH$_3$) ppm. MS (12 eV): *m*/*z* (%) = 295 (34) [M + H]$^+$, 267 (57), 239 (79), 185 (16), 157 (100). HRMS (ES-TOF): calcd. for $C_{16}H_{24}O_3P$ [M + H]$^+$ 295.1463; found 295.1468.

**Diethyl [5-(4-Nitrophenyl)pent-4-ynyl]phosphonate (3b):** Method A was employed with 1-bromo-4-nitrobenzene (153 mg, 0.6 mmol) and alkyne **3** (187 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 80:20). Yield: 100 mg (53%) of a yellow oil. IR (neat): $\tilde{\nu}$ = 2222 (C≡C), 1234 (P=O), 1023, 954 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.27 (t, $^3J$ = 7 Hz, 6 H, 2 × C$H_3$CH$_2$O), 1.80–1.95 [m, 4 H, (C$H_2$)$_2$PO], 2.51 (dt, $^4J$ = 3 Hz, $^3J$ = 6 Hz, 2 H, C$H_2$C≡C), 3.97–4.11 (m, 4 H, C$H_3$CH$_2$O), 7.42 (d, $^3J$ = 7 Hz, 2 × C$H$CCH$_3$), 7.09 (d, $^3J$ = 7.5 Hz, 2 × C$H$CC≡C) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 32.2 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, $C$H$_3$CH$_2$O), 20.6 (d, $^2J$ = 18 Hz, $C$H$_2$CH$_2$PO), 21.7 (s, $C$H$_3$Ar), 22.3 (d, $^3J$ = 4 Hz, $C$H$_2$C≡CH), 25.1 (d, $^1J$ = 142 Hz, $C$H$_2$PO), 61.8 (d, $^2J$ = 6 Hz, CH$_3C$H$_2$O), 80.6 (s, C≡$C$C$_{arom}$), 95.1 (s, $C$≡CC$_{arom}$), 123.9 (s, 2 × $C$HCNO$_2$), 131.0 (s, 2 × $C$C≡C), 132.7 (s, $C$HCC≡C), 147.1 (s, $C$NO$_2$) ppm. MS (20 eV): *m*/*z* (%) = 326 (46) [M + H]$^+$, 298 (56), 270 (100). HRMS (ES-TOF): calcd. for $C_{15}H_{21}NO_5P$ [M + H]$^+$ 326.1133; found 326.1142.

**Diethyl [5-(1,10-Phenanthrolin-3-yl)pent-4-ynyl]phosphonate (3c):** Method B was employed with 3-bromo-1,10-phenanthroline (197 mg, 0.6 mmol) and alkyne **3** (187 mg, 0.92 mmol) at reflux. A washing step with KCN was added to the workup. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 85:15). Yield: 209 mg (92%) of a yellow solid. IR (neat): $\tilde{\nu}$ = 1231 (P=O), 1020, 962 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.24 (t, $^3J$ = 7 Hz, 6 H, C$H_3$CH$_2$O), 1.77–1.95 [m, 4 H, (C$H_2$)$_2$-PO], 2.52 (dt, $^4J$ = 3 Hz, $^3J$ = 6 Hz, 2 H, C$H_2$C≡C), 3.92–4.11 (m, 4 H, C$H_3$CH$_2$O), 7.47 (dd, $^3J$ = 8 Hz, $^3J$ = 4 Hz, $H^{10}$), 7.52 (d, $^3J$ = 9 Hz, $H^7$), 7.6 (d, $^3J$ = 9 Hz, $H^6$), 8.01 (d, $^3J$ = 9 Hz, $H^9$), 8.13 (s, $H^4$), 8.92–9.03 (m, 2 H, $H^2$, $H^{11}$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 32.3 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 15.5 (d, $^3J$ = 6 Hz, $C$H$_3$CH$_2$O), 19.2 (d, $^2J$ = 18 Hz, $C$H$_2$CH$_2$PO), 20.7 (d, $^3J$ = 4 Hz, $C$H$_2$C≡CH), 23.7 (d, $^1J$ = 143 Hz, $C$H$_2$PO), 60.6 (d, $^2J$ = 6 Hz, CH$_3C$H$_2$O), 77.8 (s, C≡$C$Ar), 92.4 (s, $C$≡CAr), 118.8 (s, $C^3$), 122.2 (s, $C^{10}$), 124.3 (s, $C^7$), 126.8 (s, $C^6$), 127.4 (s, $C^8$), 128.4 (s, $C^5$), 134.9 (s, $C^9$), 136.3 (s, $C^4$), 143.2 (s, $C^{13}$), 144.7 (s, $C^{14}$), 149.5 (s, $C^{11}$), 150.0 (s, $C^{12}$) ppm. MS (20 eV): *m*/*z* (%) = 383 (39) [M + H]$^+$, 355 (24), 309 (100). HRMS (ES-TOF): calcd. for $C_{21}H_{24}N_2O_3P$ [M + H]$^+$ 383.1525; found 383.1511.

**Diethyl [5-(3-*p*-Tolylprop-2-ynyloxy)pentyl]phosphonate (8a):** Method A was employed with 4-iodotoluene (130 mg, 0.6 mmol) and alkyne **8** (241 mg, 0.92 mmol) at room temperature. Purification was effected by kugelrohr distillation (110 °C, 10 mTorr). Yield: 200 mg (95%) of a colourless oil. IR (neat): $\tilde{\nu}$ = 1237 (P=O), 1098 (C–O), 1024, 955 (P–0) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.31 (m, 6 H, 2 × C$H_3$CH$_2$O), 1.40–1.80 (m, 8 H, C$H_2$C$H_2$C$H_2$C$H_2$C$H_2$C≡C), 2.34 (s, 3 H, C$H_3$), 3.54 (t, $^3J$ = 4 Hz, 2 H, C$H_2$O), 4.02–4.14 (m, 6 H, 2 × CH$_3$C$H_2$OP, C$H_2$C≡C), 4.34 (s, 2 H, C$H_2$C≡C), 7.10 (d, $^3J$ = 7 Hz, 2 H, 2 × C$H$CCH$_3$), 7.33 (d, $^3J$ = 7.5 Hz, 2 H, 2 × C$H$CC≡C) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 33.20 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.4 (d, $^3J$ = 6 Hz, $C$H$_3$CH$_2$O), 21.4 (s, $C$H$_3$), 22.3 [d, $^3J$ = 5 Hz, $C$H$_2$(CH$_2$)$_2$PO], 25.6 (d, $^1J$ = 140 Hz, $C$H$_2$PO), 27.2 (d, $^2J$ = 17 Hz, $C$H$_2$CH$_2$PO), 29.1 (s, $C$H$_2$CH$_2$O), 58.8 (s, $C$H$_2$C≡C), 61.4 (d, $^2J$ = 5 Hz, CH$_3C$H$_2$O), 69.8 (s, $C$H$_2$OCH$_2$C≡C), 84.6 (s, C≡$C$C$_{ar}$), 86.1 (s, $C$≡CC$_{ar}$), 119.6 (s, $C$C≡C), 129.0 (s, 2 × $C$HCCH$_3$), 131.6 (s, 2 × $C$HCC≡C), 138.5 (s, $C$CH$_3$) ppm. MS (12 eV): *m*/*z* (%) = 354 (5) [M + 2H]$^+$, 353 (33) [M]$^+$, 237 (11), 208 (7.5), 207 (100), 179(10), 131 (33), 129 (72). HRMS (ES-TOF): calcd. for $C_{19}H_{30}O_4P$ [M + H]$^+$ 353.1882; found 353.1880.

**Diethyl {5-[3-(4-Nitrophenyl)prop-2-ynyloxy]pentyl}phosphonate (8b):** Method A was employed with 1-bromo-4-nitrobenzene (153 mg, 0.6 mmol) and alkyne **8** (241 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 80:20). Yield: 210 mg (91%) of a yellow oil. IR (neat): $\tilde{\nu}$ = 2237 (C≡C), 1239 (P=O), 1097 (C–O), 1027, 956 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.32 (m, 6 H, 2 × C$H_3$CH$_2$O), 1.40–1.85 (m, 8 H, C$H_2$C$H_2$C$H_2$C$H_2$CH$_2$C≡C), 3.58 (t, $^3J$ = 4 Hz, 2 H, C$H_2$O), 4.01–4.21 (m, 6 H, 2 × CH$_3$C$H_2$O, C$H_2$C≡C), 4.38 (s, 2 H, C$H_2$C≡C), 7.56 (d, $^3J$ = 9 Hz, 2 H, 2 × C$H$CC≡C), 8.18 (d, $^3J$ = 9 Hz, 2 H, 2 × C$H$CNO$_2$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 33.00 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.4 (d, $^3J$ = 6 Hz,

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2 × $CH_3CH_2O$), 22.2 [d, $^3J$ = 5 Hz, $CH_2(CH_2)_2PO$], 25.6 (d, $^1J$ = 141 Hz, $CH_2PO$), 27.1 (d, $^2J$ = 17 Hz, $CH_2CH_2PO$), 29.1 (s, $CH_2CH_2O$), 58.7 (s, $CH_2C{\equiv}C$), 61.4 (d, $^2J$ = 5 Hz, 2 × $CH_3CH_2O$), 70.2 (s, $CH_2OCH_2C{\equiv}C$), 84.1 (s, C≡$CC_{ar}$), 90.9 (s, $C{\equiv}CC_{ar}$), 123.5 (s, 2 × $CHCNO_2$), 129.6 (s, $CC{\equiv}C$), 132.5 (s, 2 × $CHCC{\equiv}C$), 147.2 (s, $CNO_2$) ppm. MS (16 eV): *m*/*z* (%) = 384 (40) $[M + H]^+$, 208 (6), 207 (100), 179 (47), 160 (17), 151 (20). HRMS (ES-TOF): calcd. for $C_{18}H_{27}NO_6P$ $[M + H]^+$ 384.1576; found 384.1557.

**Diethyl {5-[3-(1,10-Phenanthrolin-3-yl)prop-2-ynyloxy]pentyl}-phosphonate (8c):** Method B was employed with 3-bromo-1,10-phenanthroline (197 mg, 0.6 mmol) and alkyne **8** (241 mg, 0.92 mmol) at reflux. A washing step with KCN was added to the workup. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 85:15). Yield: 195 mg (74%) of a yellow solid. Method C was employed with 3-bromo-1,10-phenanthroline (197 mg, 0.6 mmol) and alkyne **8** (241 mg, 0.92 mmol) at 120 °C. A washing step with KCN was added to the workup. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 85:15). Yield: 216 mg (82%) of a yellow oil. IR (neat): ṽ = 1227 (P=O), 1099 (C–O), 1024, 958 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.34 (m, 6 H, $CH_3CH_2O$), 1.60–1.76 (m, 8 H, $CH_2CH_2CH_2CH_2CH_2C{\equiv}C$), 3.63 (t, $^3J$ = 4 Hz, 2 H, $CH_2O$), 4.3–4.12 (m, 6 H, $CH_3CH_2O$, $CH_2C{\equiv}C$), 4.44 (s, 2 H, $CH_2C{\equiv}C$), 7.66 (dd, $^3J$ = 8 Hz, $^3J$ = 4 Hz, $H^8$), 7.78 (d, $^3J$ = 9 Hz, $H^6$), 7.81 (d, $^3J$ = 9 Hz, $H5^6$), 8.25 (d, $^3J$ = 9 Hz, $H^7$), 8.32 (s, $H^4$), 9.21 (s, 2 H, $H^2$, $H^9$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 33.50 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, 6 H, $CH_3CH_2O$), 22.7 [d, $^3J$ = 5 Hz, 2 H, $CH_2(CH_2)_2PO$], 25.6 (d, $^1J$ = 155 Hz, $CH_2PO$), 27.6 (d, $^2J$ = 17 Hz, $CH_2CH_2PO$), 29.5 (s, $CH_2CH_2O$), 59.2 (s, $CH_2C{\equiv}C$), 61.9 (d, $^2J$ = 5 Hz, $CH_3CH_2O$), 70.6 (s, $CH_2OCH_2C{\equiv}C$), 83.4 (s, $CH_2C{\equiv}CH$), 90.3 (s, $CH_2C{\equiv}CH$), 119.3 (s, $C^3$), 123.7 (s, $C^8$), 126.4 (s, $C^6$), 127.7 (s, $C^5$), 128.0 (s, $C^{12}$), 129.4 (s, $C^{13}$), 136.4 (s, $C^7$), 138.9 (s, $C^4$), 145.3 (s, $C^{11}$), 146.3 (s, $C^{14}$), 151.0 (s, $C^{19}$), 152.6 (s, $C^2$) ppm. MS (22 eV): *m*/*z* (%) = 442 (25) $[M + 2H]^+$, 441 (100) $[M + H]^+$, 413 (18), 395 (19), 367 (15), 218 (8), 217 (50). HRMS (ES-TOF): calcd. for $C_{24}H_{30}N_2O_4P$ $[M + H]^+$ 441.1943; found 441.1922.

**Diethyl {2-[3-(4-Tolyl)prop-2-ynyloxy]ethyl}phosphonate (11a):** Method A was employed with 4-iodotoluene (130 mg, 0.6 mmol) and alkyne **11** (202 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 90:10). Yield: 180 mg (97%) of a colourless oil. Method C was employed with 4-bromotoluene (102 mg, 0.6 mmol) and alkyne **11** (167 mg, 0.76 mmol) at 120 °C. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 90:10). Yield: 111 mg (60%) of a colourless oil. IR (neat): ṽ = 1247 (P=O), 1093 (C–O), 1020, 955 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.32 (t, $^3J$ = 7 Hz, 6 H, 2 × $CH_3$), 2.15 (dt, $^2J$ = 26 Hz, $^3J$ = 7 Hz, 2 H, $PCH_2$), 2.34 (s, 3 H, $CH_3$), 3.84 (dt, $^3J$ = 12 Hz, 2 H, $OCH_2$), 4.11 (m, 4 H, 2 × $POCH_2CH_3$), 4.37 (s, 2 H, $OCH_2C{\equiv}CH$), 7.11 (d, $^3J$ = 7 Hz, 2 × $CHCCH_3$), 7.33 (d, $^3J$ = 7.5 Hz, 2 × $CHCC{\equiv}C$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 28.50 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, 2 × $CH_3$), 21.9 ($CH_3$), 27.3 (d, $^1J$ = 140 Hz, $PCH_2$), 59.3 (s, $OCH_2$), 62.1 (d, $^3J$ = 6 Hz, 2 × $POCH_2CH_3$), 64.3 (s, $OCH_2$), 84.3 (s, C≡$CC_{ar}$), 87.0 (s, $C{\equiv}CC_{ar}$), 119.8 (s, C≡$CC_{ar}$), 129.4 (s, 2 × $CHCCH_3$), 132.0 (s, 2 × $CHCC{\equiv}C$), 139.1 (s, $CCH_3$) ppm. MS (12 eV): *m*/*z* (%) = 311 (7) $[M + H]^+$, 310 (1) $[M]^+$, 282 (26), 225 (21), 166 (33), 138 (85), 111 (100), 91 (30), 65 (23). $C_{16}H_{23}O_4P$ (310.33): calcd. C 61.93, H 7.47; found C 61.46, H 7.84. HRMS (ES-TOF): calcd. for $C_{16}H_{23}O_4PNa$ $[M + Na]^+$ 333.1232; found 333.1236.

**Diethyl {2-[3-(4-Nitrophenyl)prop-2-ynyloxy]ethyl}phosphonate (11b):** Method A was employed with 4-iodotoluene (153 mg, 0.6 mmol) and alkyne **11** (202 mg, 0.92 mmol) at reflux. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 85:15). Yield: 184 mg (90%) of a yellow oil. IR (neat): ṽ = 1246 (P=O), 1094 (C–O), 1027, 953 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.33 (t, $^3J$ = 7 Hz, 6 H, 2 × $CH_3$), 2.14 (dt, $^2J$ = 26 Hz, $^3J_{HH}$ = 7 Hz, 2 H, $PCH_2$), 3.88 (dt, $^3J$ = 12 Hz, 2 H, $CH_2O$), 4.14 (m, 4 H, 2 × $CH_3CH_2OP$), 4.42 (d, $^4J$ = 2 Hz, 2 H, $OCH_2C{\equiv}CH$), 7.60 (d, $^3J$ = 9 Hz, 2 × $CHCC{\equiv}C$), 8.21 (d, $^3J$ = 9 Hz, 2 × $CHCNO_2$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 28.9 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, 2 × $CH_3$), 27.3 (d, $^1J$ = 142 Hz, $PCH_2$), 59.1 (s, $OCH_2$), 62.1 (d, $^3J$ = 6 Hz, 2 × $CH_3CH_2OP$), 64.7 (s, $OCH_2$), 84.9 (s, C≡$CC_{ar}$), 90.5 (s, $C{\equiv}CC_{ar}$), 124.0 (s, 2 × $CHCNO_2$), 129.7 (s, C≡C$C_{ar}$), 132.9 (s, 2 × $CHCC{\equiv}C$), 147.7 (s, $CNO_2$) ppm. MS (12 eV): *m*/*z* (%) = 343 $[M + H]^+$, 342 (100) $[M]^+$, 195 (11), 165 (18), 160 (28), 137 (15), 127 (8), 109 (6). HRMS (ES-TOF): calcd. for $C_{15}H_{21}NO_6P$ $[M + H]^+$ 342.1107; found 342.1089.

**Diethyl {2-[3-(Pyridin-4-yl)prop-2-ynyloxy]ethyl}phosphonate (11c):** Method C was employed with 4-bromopyridine hydrochloride (108 mg, 0.6 mmol) and alkyne **8** (167 mg, 0.76 mmol) at 120 °C. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 85:15). Yield: 160 mg (90%) of a yellow oil. IR (neat): ṽ = 1095 (C–O), 1020, 958 (P–0) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.34 (t, $^3J$ = 7 Hz, 6 H, 2 × $CH_3$), 2.17 (dt, $^2J$ = 26 Hz, $^3J$ = 7 Hz, 2 H, $PCH_2$), 3.86 (dt, $^3J$ = 12 Hz, 2 H, $CH_2O$), 4.08–4.16 (m, 4 H, 2 × $CH_3CH_2OP$), 4.40 (s, 2 H, $OCH_2C{\equiv}CH$), 7.33 (d, $^3J$ = 6 Hz, 2 H, 2 × $CHCC{\equiv}C$), 8.58 (d, $^3J$ = 6 Hz, 2 H, 2 × $CHN$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 28.60 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, 2 × $CH_3$), 27.3 (d, $^1J$ = 90 Hz, $PCH_2$), 59.1 (s, $OCH_2$), 62.2 (d, $^3J$ = 4 Hz, 2 × $POCH_2CH_3$), 64.6 (s, $OCH_2$), 84.3 (s, C≡$CC_{ar}$), 90.0 (s, $C{\equiv}CC_{ar}$), 126.1 (s, 2 × $CHC{\equiv}C$), 131.2 (s, C≡C$C_{ar}$), 150.1 (s, 2 × $CHN$) ppm. MS (12 eV): *m*/*z* (%) = 299 (4) $[M + 2H]^+$, 298 (38) $[M + H]^+$, 165 (100), 137 (22), 127 (55), 109 (20). HRMS (ES-TOF): calcd. for $C_{14}H_{21}NO_4P$ $[M + H]^+$ 298.1208; found 298.1209.

**Diethyl {[3-(*p*-Tolyl)prop-2-ynyloxy]methyl}phosphonate (12a):** Method B was employed with 4-iodotoluene (130 mg, 0.6 mmol) and alkyne **12** (189 mg, 0.92 mmol) at room temperature. Purification was effected by kugelrohr distillation (110 °C/10 mTorr). Yield: 170 mg (96%) of a colourless oil. Method C was employed with 4-bromotoluene (102 mg, 0.6 mmol) and alkyne **12** (156 mg, 0.76 mmol) at 120 °C. Purification was effected by kugelrohr distillation (110 °C/10 mTorr). Yield: 130 mg (74%) of a colourless oil. IR (neat): ṽ = 2125 (C≡C), 1241 (P=O), 1097 (C–O), 1019, 964 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.37 (t, $^3J$ = 7 Hz, 6 H, 2 × $CH_3$), 2.35 (s, 3 H, $CH_3$), 3.85 (d, $^2J$ = 10 Hz, 2 H, $PCH_2O$), 4.23 (m, 4 H, 2 × $CH_2OP$), 4.49 (s, 2 H, $OCH_2C{\equiv}CH$), 7.13 (d, $^3J$ = 7 Hz, 2 H, 2 × $CHCCH_3$), 7.56 (d, $^3J$ = 7.5 Hz, 2 H, 2 × $CHCC{\equiv}C$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 22.60 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, 2 × $CH_3$), 21.9 ($CH_3$), 61.2 (d, $^2J$ = 14 Hz, 2 × $CH_3CH_2OP$), 62.9 (d, $^3J$ = 6 Hz, $OCH_2$), 63.2 (d, $^1J$ = 168 Hz, $PCH_2O$), 83.3 (s, C≡$CC_{ar}$), 88.1 (s, $C{\equiv}CC_{ar}$), 119.5 (s, $C_{ar}C{\equiv}C$), 129.5 (s, 2 × $CHCCH_3$), 132.1 (s, 2 × $CHCC{\equiv}C$), 139.3 (s, $CCH_3$) ppm. MS (14 eV): *m*/*z* (%) = 297 (15) $[M + H]^+$, 130 (5), 129 (100). $C_{15}H_{21}O_4P$ (296.30): calcd. C 60.80, H 7.14; found C 60.85, H 7.08. HRMS (ES-TOF): calcd. for $C_{15}H_{22}O_4P$ $[M + H]^+$ 297.1256; found 297.1246.

**Diethyl {[3-(4-Nitropheny)prop-2-ynyloxy]methyl}phosphonate (12b):** Method A was employed with 1-bromo-4-nitrobenzene

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(153 mg, 0.6 mmol) and alkyne **12** (189 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 85:15). Yield: 188 mg (97%) of a yellow oil. IR (neat): $\tilde{\nu}$ = 1236 (P=O), 1014, 964 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.37 (t, $^3J$ = 7 Hz, 6 H, 2 × C$H_3$), 3.94 (d, $^2J$ = 10 Hz, 2 H, PC$H_2$O), 4.21 (m, 4 H, 2 × $CH_3CH_2$OP), 4.55 (d, $^2J$ = 2 Hz, 2 H, OC$H_2$C≡CH), 7.59 (d, $^3J$ = 9 Hz, 2 H, 2 × C*H*CC≡C), 8.20 (d, $^3J$ = 9 Hz, 2 H, 2 × C*H*$CNO_2$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 22.80 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (d, $^3J$ = 6 Hz, 2 × *C*$H_3$), 61.0 (d, $^2J$ = 13 Hz, 2 × *C*$H_2$OP), 63.0 (d, $^3J$ = 6 Hz, O*C*$H_2$), 63.9 (d, $^1J$ = 167 Hz, P*C*$H_2$O), 86.0 (s, C≡*C*$C_{ar}$), 89.5 (s, *C*≡$CC_{ar}$), 124.0 (s, 2 × *C*H$CNO_2$), 129.4 (s, *C*$_{ar}$C≡C), 132.9 (s, 2 × *C*HCC≡C), 147.7 (s, *C*$NO_2$) ppm. MS (10 eV): *m*/*z* (%) = 329 (13) $[M + H]^+$, 328 (100) $[M]^+$, 300 (30), 272 (21), 181 (5), 178 (10), 160 (38), 151 (9). HRMS (ES-TOF): calcd. for $C_{14}H_{18}NO_6PNa$ $[M + Na]^+$ 350.0769; found 350.0776.

**Diethyl {[3-(Pyridin-4-yl)prop-2-ynyloxy]methyl}phosphonate (12c):** Method C was employed with 4-bromopyridine hydrochloride (108 mg, 0.6 mmol) and alkyne **12** (156 mg, 0.76 mmol) at 120 °C. Yield: 108 mg (64%) of a yellow oil. IR (neat): $\tilde{\nu}$ = 1230 (P=O), 1100 (C–O), 1027, 960 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.36 (t, $^3J$ = 7 Hz, 6 H, 2 × C$H_3$), 3.95 (d, $^2J$ = 9 Hz, 2 H, PC$H_2$O), 4.23 (m, 4 H, 2 × C$H_2$OP), 4.53 (s, 2 H, OC$H_2$C≡CH), 7.30 (d, $^3J$ = 6 Hz, 2 H, 2 × C*H*$CCH_3$), 8.59 (d, $^3J$ = 6 Hz, 2 H, 2 × C*H*CC≡C) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 22.8 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 15.3 (d, $^3J$ = 5 Hz, 2 × *C*$H_3$), 59.4 (d, $^2J$ = 14 Hz, 2 × $CH_3$*C*$H_2$OP), 61.4 (d, $^3J$ = 6 Hz, O*C*$H_2$), 62.3 (d, $^1J$ = 166 Hz, P*C*$H_2$O), 83.6 (s, C≡*C*$C_{ar}$), 87.5 (s, *C*≡$CC_{ar}$), 124.5 (s, 2 × *C*H), 129,4 (s, *C*$_{ar}$C≡C), 148.6 (s, 2 × *C*HN) ppm. MS (12 eV): *m*/*z* (%) = 299 (4) $[M + 2H]^+$, 298 (38) $[M + H]^+$, 165 (100), 137 (22), 127 (55), 109 (20). HRMS (ES-TOF): calcd. for $C_{13}H_{19}NO_4P$ $[M + H]^+$ 284.1052; found 284.1061.

**Diethyl {[3-(1,10-Phenanthrolin-3-yl)prop-2-ynyloxy]methyl}phosphonate (12d):** Method B was employed with 3-bromo-1,10-phenanthroline (197 mg, 0.6 mmol) and alkyne **12** (189 mg, 0.92 mmol) at reflux. A washing step with KCN was added to the workup. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 90:10). Yield: 180 mg (78%) of an orange solid. IR (neat): $\tilde{\nu}$ = 1226 (P=O), 1099 (C–O), 1024, 957 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.38 (t, $^3J$ = 7 Hz, 6 H, 2 × C$H_3$), 4.01 (d, $^2J$ = 9 Hz, 2 H, PC$H_2$O), 4.23 (m, 4 H, 2 × C$H_2$OP), 4.62 (s, 2 H, *OCH*$_2$*C*≡CH), 7.65 (dd, $^3J$ = 8 Hz, $^3J$ = 4 Hz, *H*$^8$), 7.75 (d, $^3J$ = 9 Hz, *H*$^6$), 7.82 (d, $^3J$ = 9 Hz, *H*$^5$), 8.26 (d, $^3J$ = 9 Hz, *H*$^7$), 8.31 (s, *H*$^4$), 9.19 (s, 2 H, *H*$^2$, *H*$^9$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 22.16 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.1 (d, $^3J$ = 6 Hz, 2 × *C*$H_3$), 60.4 (d, $^2J$ = 9 Hz, 2 × *C*$H_2$OP), 62.3 (d, $^3J$ = 6 Hz, O*C*$H_2$), 63.2 (d, $^1J$ = 144 Hz, P*C*$H_2$O), 84.2 (s, C≡*C*H), 87.9 (s, *C*≡CH), 118.9 (s, *C*$^3$), 123.0 (s, *C*$^8$), 125.6 (s, *C*$^6$), 127.1 (s, *C*$^5$), 127.2 (s, *C*$^{12}$), 128.7 (s, *C*$^{13}$), 135.7 (s, *C*$^7$), 138.2 (s, *C*$^4$), 144.8 (s, *C*$^{11}$), 145.5 (s, *C*$^{14}$), 150.3 (s, *C*$^9$), 151.7 (s, *C*$^2$) ppm. MS (12 eV): *m*/*z* (%) = 386 (8) $[M + H]^+$, 385 (25) $[M]^+$, 357 (17), 329 (8), 311 (45), 281 (15), 219 (17), 217 (100). HRMS (ES-TOF): calcd. for $C_{20}H_{22}N_2O_4P$ $[M + H]^+$ 385.1317; found 385.1306.

**Tetraethyl {Methyl[3-(*p*-tolyl)prop-2-ynyl]methylene}diphosphonate (14a):** Method A was employed with 4-iodotoluene (130 mg, 0.6 mmol) and alkyne **14** (312 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 85:15). Yield: 232 mg (90%) of a colourless oil. IR (neat): $\tilde{\nu}$ = 1235 (P=O), 1015, 960 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.33 (t, $^3J$ = 7 Hz, 12 H, 4 × C$H_3$$CH_2$O), 1.62 (t, $^3J$ = 16 Hz, 3 H, C$H_3$), 2.33 (s, 3 H, C$H_3$), 3.02 (t, $^2J$ = 15 Hz, 2 H, C$H_2$C≡C), 4.02–4.28 (m, 8 H, 4 × $CH_3$C$H_2$O), 7.05 (d, $^3J$ = 7 Hz, 2 H, 2 × C*H*$CCH_3$), 7.30 (d, $^3J$ = 7 Hz, 2 H, 2 × C*H*CC≡C) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 26.50 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.8 (t, $^3J$ = 3 Hz, 4 × *C*$H_3$), 17.1 (t, $^2J$ = 6 Hz, *C*$H_3$), 21.8 (s, *C*$H_3$), 24.4 (t, $^3J$ = 4 Hz, C$H_2$C≡C), 40.9 (t, $^1J$ = 135 Hz, P*C*P), 63.3 (d, $^3J$ = 4 Hz, 4 × PO*C*$H_2$), 83.7 (s, C≡*C*$C_{ar}$), 84.8 (s, *C*≡$CC_{ar}$), 120.9 (s, *C*C≡C), 129.3 (s, 2 × *C*H$CCH_3$), 131.7 (s, 2 × *C*HCC≡C), 138.2 (s, *C*$CH_3$) ppm. MS (16 eV): *m*/*z* (%) = 431 (28) $[M + H]^+$, 404 (14), 403 (100), 375 (62), 347 (23), 319 (8). HRMS (ES-TOF): calcd. for $C_{20}H_{33}O_6P_2$ $[M + H]^+$ 431.1752; found 431.1743.

**Tetraethyl {Methyl-[3-(4-nitrophenyl)prop-2-ynyl]methylene}diphosphonate (14b):** Method A was employed with 1-bromo-4-nitrobenzene (153 mg, 0.6 mmol) and alkyne **14** (312 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 80:20). Yield: 251 mg (91%) of a yellow oil. IR (neat): $\tilde{\nu}$ = 1235 (P=O), 1013, 962 (P–0) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.35 (t, $^3J$ = 7 Hz, 12 H, 4 × C$H_3$$CH_2$O), 1.53 (t, $^3J$ = 16 Hz, 3 H, C$H_3$), 2.92 (t, $^2J$ = 15 Hz, 2 H, C$H_2$C≡C), 4.02–4.28 (m, 8 H, 4 × $CH_3$C$H_2$O), 7.45 (d, $^3J$ = 9 Hz, 2 H, 2 × C*H*CC≡C), 8.15 (d, $^3J$ = 9 Hz, 2 H, 2 × C*H*$CNO_2$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 25.20 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.3–16.9 (t, $^3J$ = 3 Hz, 4 × *C*$H_3$), 17.0 (t, $^2J$ = 6 Hz, *C*$H_3$), 24.3 (t, $^3J$ = 4 Hz, C$H_2$C≡C), 40.3 (t, $^1J$ = 135 Hz, P*C*P), 63.0 (d, $^3J$ = 4 Hz, 4 × PO*C*$H_2$), 81.8 (s, C≡*C*$C_{ar}$), 91.6 (s, *C*≡$CC_{ar}$), 123.5 (s, 2 × *C*H$CNO_2$), 130.6 (s, *C*C≡C), 132.2 (s, 2 × *C*HCC≡C), 146.7 (s, *C*$NO_2$) ppm. MS (20 eV): *m*/*z* (%) = 462 (20) $[M + H]^+$, 434 (29), 406 (47), 378 (70), 350 (100). HRMS (ES-TOF): calcd. for $C_{19}H_{30}NO_8P_2$ $[M + H]^+$ 462.1447; found 462.1440.

**Tetraethyl {Methyl[3-(1,10-phenanthrolin-3-yl)prop-2-ynyl]methylene}diphosphonate (14c):** Method B was employed with 3-bromo-1,10-phenanthroline (197 mg, 0.6 mmol) and alkyne **14** (312 mg, 0.92 mmol) at reflux. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 90:10), affording compound **14c** (248 mg, 80% yield, yellow solid) and compound **14d** (30 mg, 9% yield). IR (neat): $\tilde{\nu}$ = 2235 (C≡C), 1235 (P=O), 1097 (C–O), 1014, 962 $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.29 (t, $^3J$ = 7 Hz, 12 H, 4 × C$H_3$$CH_2$O), 1.57 (t, $^3J$ = 16 Hz, 3 H, C$H_3$), 3.05 (t, $^2J$ = 15 Hz, 2 H, C$H_2$C≡C), 4.05–4.26 (m, 8 H, 4 × $CH_3$C$H_2$O), 7.48 (dd, $^3J$ = 8 Hz, $^3J_{HH}$ = 4 Hz, *H*$^8$), 7.59 (d, $^3J$ = 9 Hz, *H*$^6$), 7.65 (d, $^3J$ = 9 Hz, *H*$^5$), 8.10 (d, $^3J$ = 9 Hz, *H*$^7$), 8.16 (s, *H*$^4$), 9.03 (m, 2 H, *H*$^2$, *H*$^9$) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 24.5 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.4 (t, $^3J$ = 3 Hz, 4 × *C*$H_3$), 16.9 (t, $^2J$ = 6 Hz, *C*$H_3$), 24.24 (t, $^3J$ = 4 Hz, C$H_2$C≡C), 40.3 (t, $^1J$ = 135 Hz, P*C*P), 62.9 (m, $^3J$ = 4 Hz, 4 × PO*C*$H_2$), 80.2 (s, C≡*C*$C_{ar}$), 90.1 (t, $^3J$ = 5 Hz, *C*≡$CC_{ar}$), 119.8 (s, *C*$^3$), 123.1 (s, *C*$^8$), 125.3 (s, *C*$^6$), 127.1 (s, *C*$^5$), 127.6 (s, *C*$^{12}$), 128.7 (s, *C*$^{13}$), 135.9 (s, *C*$^7$), 137.9 (s, *C*$^4$), 144.4 (s, *C*$^{11}$), 146.02 (s, *C*$^{14}$), 150.4 (s, *C*$^9$), 152.0 (s, *C*$^2$) ppm. MS (20 eV): *m*/*z* (%) = 519 (20) $[M + H]^+$, 491 (9), 463 (8), 445 (22), 417 (88), 389 (50), 381 (100), 353 (68), 325 (41), 309 (37). HRMS (ES-TOF): calcd. for $C_{25}H_{33}N_2O_6P_2$ $[M + H]^+$ 519.1814; found 519.1793.

**Octaethyl (Dec-4,6-diynyl)-2,2,9,9-tetraphosphonate (14d):** IR (neat): $\tilde{\nu}$ = 1233 (P=O), 1012, 943 (P–O) $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.34 (t, $^3J$ = 7 Hz, 16 H, 8 × C$H_3$$CH_2$O), 1.53 (t, $^3J$ = 16 Hz, 6 H, 2 × C$H_3$), 2.89 (t, $^2J$ = 15 Hz, 4 H, 2 × C$H_2$C≡C), 4.17–4.22 (m, 24 H, 8 × $CH_3$C$H_2$O) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 26.50 ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.4 ($s_{large}$, 8 × *C*$H_3$), 23.8 (t, $^2J$ = 6 Hz, 2 × *C*$H_3$), 23.8 (t, $^3J$ = 4 Hz, C$H_2$C≡C), 40.1 (t, $^1J$ = 135 Hz, P*C*P), 63.0 (m, 8 × PO*C*$H_2$), 68.1 (s, $CH_2$C≡*C*), 72.8 (t, $^3J$ = 10 Hz, 2 × $CH_2$*C*≡C) ppm. MS (21 eV):

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*m/z* (%) = 679 (32) $[M + H]^+$, 651 (100), 623 (90), 595 (46), 567 (26), 539 (15). HRMS (ES-TOF): calcd. for $C_{26}H_{51}O_{12}P_4$ $[M + H]^+$ 679.2331; found 679.2361.

**Hexaethyl [5-(*p*-Tolyl)pent-4-ynyl]-1,2,2-triphosphonate (16a):** Method A was employed with 4-iodotoluene (130 mg, 0.6 mmol) and alkyne **IV** (437 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 85:15). Yield: 435 mg (77%) of a yellow oil. IR (neat): $\tilde{\nu}$ = 1241 (P=O), 1016, 946 (P–O), 793, 706 $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.29–1.38 (m, 18 H, 6 × C*H*$_3$CH$_2$O), 2.33 (s, 3 H, C*H*$_3$), 2.50–2.71 (m, 2 H, C*H*$_2$P), 3.39 (t, $^2J$ = 15 Hz, 2 H, C*H*$_2$C≡C), 4.11–4.28 (m, 12 H, 6 × CH$_3$C*H*$_2$O), 7.08 (d, $^3J$ = 7 Hz, 2 H, 2 × C*H*CCH$_3$), 7.35 (d, $^3J$ = 7 Hz, 2 H, 2 × C*H*CC≡C) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 22.9 (d, $^3J$ = 42 Hz, *P*CP), 22.8 (d, $^3J$ = 44 Hz, *P*CP), 25.5 (dd, $^3J$ = 47 Hz, $^3J$ = 44 Hz, CH$_2$*P*) ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.2–16.3 (m, 6 × *C*H$_3$), 18.9 (s, *C*H$_3$), 21.3 (s, C*H*$_2$C≡C), 26.2 (d, $^1J$ = 143 Hz, P*C*H$_2$), 43.1 (t, $^1J$ = 133 Hz, P*C*P), 61.8 (d, $^3J$ = 6 Hz, 2 × PO*C*H$_2$), 63.0–63.3 (m, 4 × PO*C*H$_2$), 83.9 (s, C≡*C*C$_{ar}$), 84.5 (s, *C*≡CC$_{ar}$), 120.6 (s, *C*C≡C), 128.8 (s, 2 × *C*HCCH$_3$), 131.3 (s, 2 × *C*HCC≡C), 137.6 (s, *C*CH$_3$) ppm. MS (16 eV): *m/z* (%) = 431 (28) $[M + H]^+$, 403 (100), 375 (63), 347 (24), 319 (8). HRMS (ES-TOF): calcd. for $C_{24}H_{42}O_9P_3$ $[M + H]^+$ 567.2042; found 567.2048.

**Hexaethyl [5-(4-Nitrophenyl)pent-4-ynyl]-1,2,2-triphosphonate (16b):** Method A was employed with 1-bromo-4-nitrobenzene (153 mg, 0.6 mmol) and alkyne **IV** (437 mg, 0.92 mmol) at room temperature. Purification was effected by chromatography on silica gel (dichloromethane/methanol, 80:20). Yield: 344 mg (96%) of a yellow oil. IR (neat): $\tilde{\nu}$ = 2223 (C≡C), 1240 (P=O), 1016, 962 (P–O), 796, 751 $cm^{-1}$. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta$ = 1.25–1.39 (m, 18 H, 6 × C*H*$_3$CH$_2$O), 2.50–2.71 (m, 2 H, C*H*$_2$P), 3.46 (t, $^2J$ = 15 Hz, 2 H, C*H*$_2$C≡C), 4.11–4.31 (m, 12 H, 6 × CH$_3$C*H*$_2$O), 7.60 (d, $^3J$ = 7 Hz, 2 × C*H*CNO$_2$), 8.17 (d, $^3J$ = 7 Hz, 2 × C*H*CC≡C) ppm. $^{31}P$ NMR (101.25 MHz, $CDCl_3$): $\delta$ = 22.4 (d, $^3J$ = 42 Hz, *P*CP), 23.1 (d, $^3J$ = 44 Hz, *P*CP), 25.0 (dd, $^3J$ = 40 Hz, $^3J$ = 45 Hz, CH$_2$*P*) ppm. $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta$ = 16.1–16.3 (m, 6 × *C*H$_3$), 21.7 (s, C*H*$_2$C≡C), 26.2 (d, $^1J$ = 140 Hz, P*C*H$_2$), 42.7 (t, $^1J$ = 112 Hz, P*C*P), 61.8 (d, $^3J$ = 7 Hz, 2 × PO*C*H$_2$), 63.0–63.4 (m, 4 × PO*C*H$_2$), 82.3 (s, C≡*C*C$_{ar}$), 91.7 (s, *C*≡CC$_{ar}$), 123.3 (s, 2 × *C*HCNO$_2$), 130.5 (s, 2 × *C*C≡C), 132.0 (s, 2 × *C*HCC≡C), 146.6 (s, *C*NO$_2$) ppm. MS (20 eV): *m/z* (%) = 462 (15) $[M + H]^+$, 434 (20), 406 (38), 378 (75), 350 (100). HRMS (ES-TOF): calcd. for $C_{23}H_{39}NO_{11}P_3$ $[M + H]^+$ 598.1736; found 598.2048.

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