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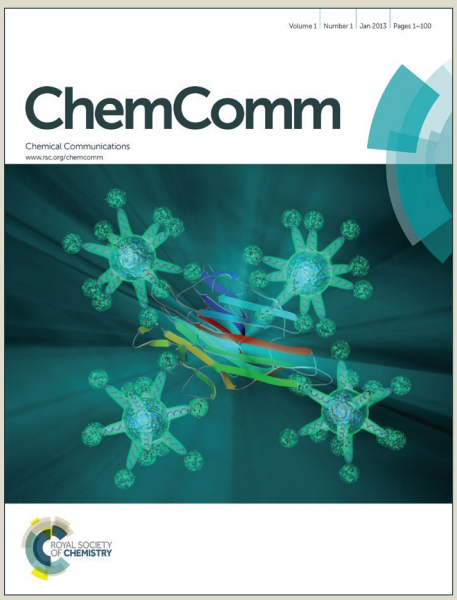

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A one-pot strategy to β-ketophosphonates: sliver/copper catalyzed direct oxyphosphorylation of alkynes with *H*-phosphonates and oxygen in the air

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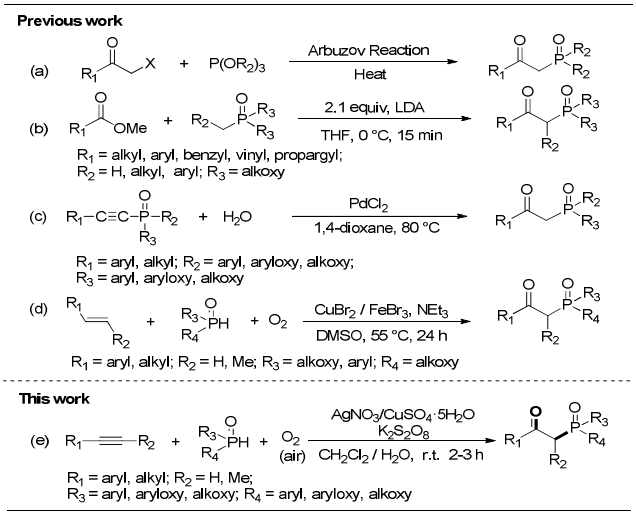
A highly efficient one-pot strategy has been developed for the synthesis of β-ketophosphonates directly from alkynes and dialkyl *H*-phosphonates in the presence of widely available $AgNO_3/CuSO_4$ and $K_2S_2O_8$ at room temperature under open-air conditions.

β-ketophosphonates are extremely versatile intermediates in organic chemistry, especially for the construction of α,β-unsaturated carbonyl compounds through the well-known Horner-Wadsworth-Emmons (HWE) reactions.[1] β-ketophosphonates exhibit a wide range of biological activities and outstanding metal-complexing abilities.[2] β-ketophosphonates can therefore be used for liquid-liquid extraction of metal ions.[3] In addition, β-ketophosphonates can serve as useful precursors in the synthesis of chiral β-amino and β-hydroxy phosphonic acids as well, both of which are endowed with interesting biological properties.[4] Recently, Nishibayashi's group reported that, in the presence of catalytic amounts of copper (II) and an optically active ligand, trifluoromethanesulfonate can undergo enantioselective alkylation with diaryl methanols to form α-alkyl-β-ketophosphonates with a high enantioselectivity.[5] By employing a palladium complex as chiral catalyst, Kim's group accomplished a highly efficient enantioselective fluorination of various α-chloro-β-ketophosphonates with excellent yield and enantioselectivity, etc.[6]

Generally, β-ketophosphonates are prepared by the reaction of α-haloketones with trialkylphosphites (Arbuzov Reaction) (Scheme 1a)[7] or acylation of alkylphosphonates with carboxylic acid derivatives by employing stoichiometric amounts of organometallic reagents (Scheme 1b).[8] Alternative procedures include oxidation of β-hydroxyalkylphosphonates with inorganic oxidants,[9] acylation of arenes with phosphonoacetic acids,[10] and metal-mediated reactions of α-halophosphonates with esters,[11] and so on.[12] However, almost all of these methods suffer from limitations such as low atom economy, inaccessible materials, tedious procedures, relatively harsh reaction conditions and excess amounts of organometallic reagents. Recently, two methodologies about hydration of alkynylphosphonates to β-ketophosphonates have been developed, in which, relatively expensive palladium(II) (Scheme 1c) and gold(I) catalysts were employed to catalyse the corresponding hydration reactions, respectively.[13] The disadvantage of these methods is that one must synthesize the starting materials, alkynylphosphonates in advance, using previously published methods.[14] In contrast, Ji's group introduced a relatively mild method to access β-ketophosphonates, through direct oxyphosphorylation of alkenes with dioxygen and *H*-phosphonates in the presence of Cu-Fe cocatalysts.[15] However Ji's method still suffers from several drawbacks such as long reaction time (24 h), oxygen atomosphere, and relatively poor product yields (Scheme 1d). Therefore, development of convenient, efficient, and especially benign methods to access β-ketophosphonates is still highly desirable in synthetic chemistry.

Herein, we disclose a more convenient synthetic approach by which a series of β-ketophosphonates are readily prepared by direct one-pot reaction of alkynes with dialkyl *H*-phosphonates and oxygen in the air in the presence of silver/copper catalysts and $K_2S_2O_8$ at room temperature. This work is interesting because of the direct oxyphosphonylation that can be performed without the need to prepare alkynylphosphonates.[13, 14] The methodology is an extension of the work of the Zhao group,[13] however this procedure is more powerful. Compared to Ji's method, the most prominent advantages of our method include a much reduced reaction time (2-3 hours), open air and room temperature reaction conditions, and excellent product yields.



Scheme 1. Comparison of previous work with this work

We initiated the meaningful study, starting with establishing optimal experimental conditions using the model reaction of phenylacetylene (**1a**) with diethyl phosphonate (**2a**) under open-air conditions for 3 h at room temperature. The screening results

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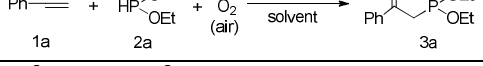
are summarized in Table 1. Initially, the reaction of phenylacetylene (**1a**) with diethyl phosphonate (**2a**) was performed in CH_2Cl_2-H_2O (v/v = 1/1) to examine the catalytic activities of several relatively cheap transition-metal salts including Fe, Ag, Cu and Mg salts (Table 1, entries 1-11). The reluts showed that metal salts such as $FeCl_3$•$6H_2O$ and $Fe(NO_3)_3$ failed to give the product **3a** (Table 1, entries 1-2). Among the silver salts (Table 1, entries 3-5), $AgNO_3$ was found to be the most effective catalyst. Notably, the yield increased tremendously when $CuSO_4$•$5H_2O$ was employed as the cocatalyst of $AgNO_3$ in the presence of $K_2S_2O_8$ (Table 1, entry 6). Other transition metal salts, such as $Cu(OAc)_2$, CuI, CuBr, $FeSO_4$ and $MgSO_4$ were less effective (Table 1, entries 7-11). It is worth noting that the model reaction failed to give the product **3a** when metals or $K_2S_2O_8$ were absent (Table 1, entries 12, 13). And also $CuSO_4$•$5H_2O$ alone cannot serve as a catalyst (Table 1, entry 14). Besides $K_2S_2O_8$, other oxidants such as TBHP, DTBP, H_2O_2 and m-CPBA were also examined. The result showed that those oxidants failed to produce the product **3a** (entries 15-18). Thus the metal catalysts and $K_2S_2O_8$ were indispensable for the reaction. The solvent systems employed also notably affected the related reaction efficiencies. Conducting the reaction in DMSO-H_2O, CH_3CN-H_2O and acetone-H_2O failed to generate the product **3a** (Table 1, entries 19-21), while the reaction conducted in $CHCl_3$-H_2O gave a moderate yield (entry 22). The investigations of solvent systems (Table 1, entries 19-22) indicated that CH_2Cl_2-H_2O (v/v = 1/1) shown in entry 6 still brought about the best result. Suitable amounts of $AgNO_3$, $CuSO_4$•$5H_2O$ and $K_2S_2O_8$ were also extensively screened (Table 1, entries 23-30). The amounts shown in entry 29 bought about the most satisfying yield. Therefore the best yield of **3a** (92.1%) was obtained by employing 5.0 mol% $AgNO_3$, 10.0 mol% $CuSO_4$•$5H_2O$ and 4 equivalent of $K_2S_2O_8$ in CH_2Cl_2-H_2O at room temperature for 3 h (Table 1, entry 29).

Table 1 Optimization of reaction conditions.[a]



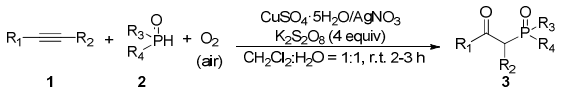
1a 2a 3a

Entry	Catalyst (mol%)	Cocatalyst (mol%)	oxidant (equiv)	Solvent	Yield(%)[b]
1	$FeCl_3·6H_2O$(10.0)	———	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	0
2	$Fe(NO_3)_3$(10.0)	———	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	0
3	Ag_2CO_3(10.0)	———	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	9
4	AgOAc(10.0)	———	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	19
5	$AgNO_3$(10.0)	———	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	37
6	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	86
7	$AgNO_3$(10.0)	$Cu(OAc)_2$(15.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	62
8	$AgNO_3$(10.0)	CuI(15.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	13
9	$AgNO_3$(10.0)	CuBr(15.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	30
10	$AgNO_3$(10.0)	$FeSO_4$(15.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	trace
11	$AgNO_3$(10.0)	$MgSO_4$(15.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	43
12	——-	———	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	0
13	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	———	CH_2Cl_2/H_2O	0
14	——-	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	0
15	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	TBHP(4)	CH_2Cl_2/H_2O	0
16	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	DTBP(4)	CH_2Cl_2/H_2O	0
17	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	H_2O_2(4)	CH_2Cl_2/H_2O	0
18	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	m-CPBA(4)	CH_2Cl_2/H_2O	0
19	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(4)	DMSO/H_2O	0
20	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(4)	CH_3CN/H_2O	0
21	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(4)	acetone/H_2O	0
22	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(4)	$CHCl_3/H_2O$	69
23	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(5)	CH_2Cl_2/H_2O	83
24	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(3)	CH_2Cl_2/H_2O	75
25	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (15.0)	$K_2S_2O_8$(2)	CH_2Cl_2/H_2O	70
26	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (5.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	60
27	$AgNO_3$(10.0)	$CuSO_4·5H_2O$ (10.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	87
28	$AgNO_3$(2.5)	$CuSO_4·5H_2O$ (10.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	85
29	**$AgNO_3$(5.0)**	**$CuSO_4·5H_2O$ (10.0)**	**$K_2S_2O_8$(4)**	**CH_2Cl_2/H_2O**	**92**
30	$AgNO_3$(7.5)	$CuSO_4·5H_2O$ (10.0)	$K_2S_2O_8$(4)	CH_2Cl_2/H_2O	89

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), catalyst, cocatalyst, oxidant and 5.0 mL of mixed solvent (v/ v = 1/ 1) at room temperature for 3 h. [b] Determined by ^{31}P NMR.

The substrate scope of alkynes and dialkyl *H*-phosphonates under the optimized conditions was then examined. As demonstrated in Table 2. A large variety of β-ketophosphonates was conveniently and efficiently obtained via this novel silver/copper catalyzed reaction. In general, both electro-rich and electro-deficient aromatic alkynes were suitable for this protocol. Starting from phenylacetylene and its ring-substituted derivatives, the corresponding β-ketophosphonates were obtained in good to excellent yields (**3a-q**). Propargyl aryl ethers, which could be thought of a type of aliphatic alkynes, were also well suitable for the reaction, affording the expected β-ketophosphonates (**3r-x**) in moderate to good yield. In addition, the method smoothly and efficiently transformed two other aliphatic alkynes, cyclopropyl acetylene and 1-hexyne, to the corresponding β-ketophosphonates (**3y-z**). In comparison with the method developed by Ji's group,[15] our substrate scope of alkynes successfully extended to aliphatic alkynes. Also, an internal aromatic alkyne was tolerated in this process, leading to the desired product **3aa** in a moderate yield. It can be seen here that the electronic effects of substituents attached benzene ring had little influence on the efficiency of oxyphosphorylation reactions (**3e-q**, **3u-x**). Moreover, owing to the mildness of the reaction conditions employed, the cyclopropyl group (**3y**), a functionally unstable group, survived the reaction unchanged. With respect to organophosphorous reagents employed, in addition to **2a**, diisopropyl *H*-phosphonate (**2b**), diphenylphosphine oxide (**2c**) and ethyl phenylphosphinate (**2d**) were all suitable substrates, leading to the products **3b-d**, **f-h**, **j**, **n**, **p**, **q**, **s**, **t**, **v**, **w** and **x** in good to excellent yields.

Table 2 Scope of the oxyphosphorylation of alkynes.[a, b]



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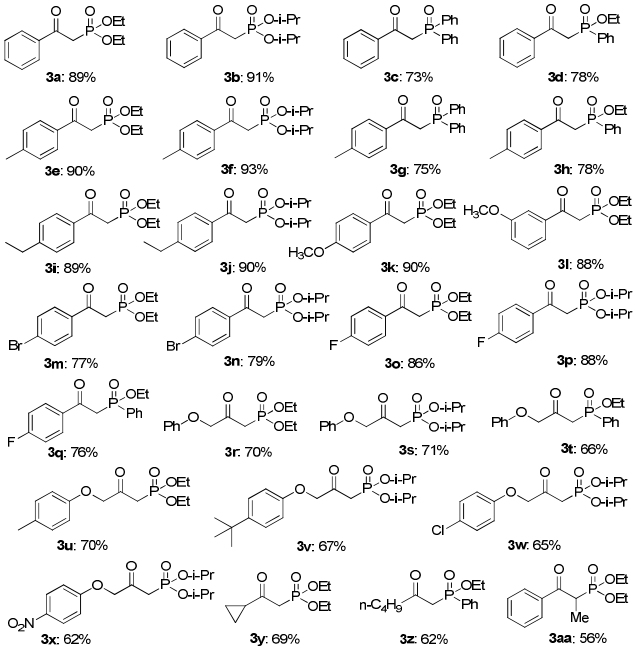

[a] Reaction conditions: **1a-z** (0.3 mmol), **2a-d** (0.45 mmol), $AgNO_3$ (5.0 mol%), $CuSO_4·5H_2O$ (10.0 mol%), $K_2S_2O_8$ (4 equiv), CH_2Cl_2/H_2O (v/ v = 1/ 1) 5.0 mL at room temperature for 3 h. [b] Isolated yield.

Two more synthetic experiments were subsequently carried out to deepen our understanding of the mechanism (Scheme 3). When TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), a widely used radical scavenger, was added into the reaction system,

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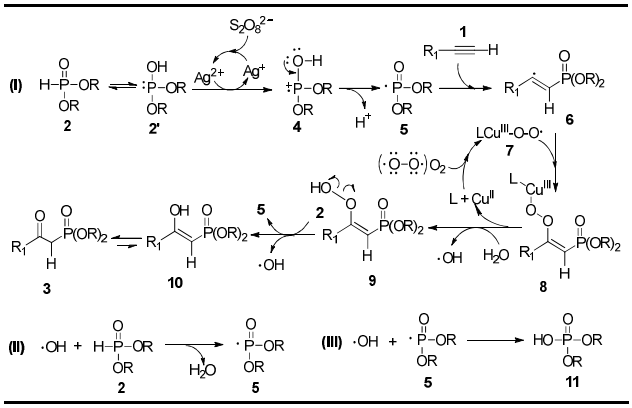
oxyphosphorylation reaction of phenylacetylene **1a** with diethyl *H*-phosphonate **2a** was quenched (Scheme 3-a), suggesting that the reactions proceed via a radical mechanism. When the reaction was carried out under a nitrogen atmosphere, the corresponding β-ketophosphonates **3a** was not obtained (Scheme 3-b), indicating that the copper/silver-catalyzed oxyphosphorylation of alkynes required the presence of oxygen. A plausible mechanism is proposed accordingly in Scheme 2. The dialkyl *H*-phosphonate $(RO)_2P(O)H$ **2** exists in equilibrium with its tautomer dialkyl phosphite $(RO)_2POH$ **2'**.[16] Initially, Ag(I) cation is oxidized to Ag(II) cation by peroxodisulfate.[16b, 17] Then diethyl phosphite **2'** is deprived of an electron by the Ag(II) ion, forming cation radical **4**, which subsequently loses a proton, giving phosphite radical **5**.[16b, c, 18] This process is similar to that proposed by Huang's group.[16b] The resulting radical **5** selectively adds to alkyne **1**, leading to an alkenyl radical **6**. Oxygen is one of the most important radicals. Molecular oxygen in the ground state is a diradical with one unpaired electron on each oxygen. It is well known that the copper active-oxygen complexes have been demonstrated or suggested to be involved in copper proteins (enzymes), playing key roles in the oxygen transport and the oxidation/oxygenation reactions in biological systems, being one of the most attractive research objectives of bioinorganic chemistry. The copper active oxygen species are also very important intermediates involved in a variety of copper-catalyzed reactions in synthetic organic reactions.[19, 20] O_2 here reacts further with the copper (II) to form an active-oxygen copper complex **7**. The alkenyl radical **6** is then attacked by this active-oxygen copper complex **7**, affording complex **8**. Complex **8** quickly reacts with water, forming hydroperoxide **9** and a copper(II) ion. The oxygen-oxygen bond of the hydroperoxide of **9** is quite weak, and it breaks and produces radicals that can



Scheme 2 Proposed reaction mechanism

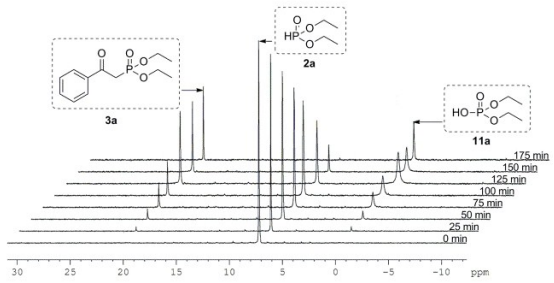
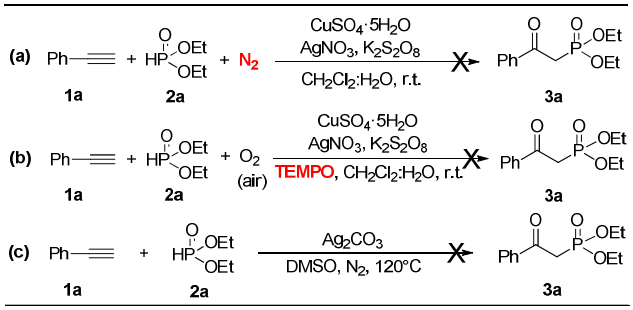


Figure 1 ^{31}P NMR stacks diagram for Scheme 2. Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $AgNO_3$ (5.0 mol%), $CuSO_4•5H_2O$ (10.0 mol%), $K_2S_2O_8$ (4 equiv), CH_2Cl_2-H_2O (v/v = 1/1) (5.0 mL) at room temperature for 3 h. The whole process was monitored by ^{31}P NMR every 25 min (comp-**2a**, 7.1 ppm; comp-**3a**, 20.6 ppm; comp-**11a**, -0.8 ppm).



Scheme 3 Preliminary mechanistic studies. Reaction conditions: (a) **1a** (0.3 mmol), **2a** (0.45 mmol), $AgNO_3$ (5.0 mol%), $CuSO_4•5H_2O$ (10.0 mol%), $K_2S_2O_8$ (4 equiv), CH_2Cl_2-H_2O (v/v = 1/1) (5.0 mL) under nitrogen atmosphere for 3 h at room temperature; (b) **1a** (0.3 mmol), **2a** (0.45 mmol), $AgNO_3$ (5.0 mol%), $CuSO_4•5H_2O$ (10.0 mol%), $K_2S_2O_8$ (4 equiv), CH_2Cl_2-H_2O (v/v = 1/1) (5.0 mL), TEMPO (3 equiv) at room temperature for 3 h.

initiate other chain reactions. Via initial homolysis of the oxygen-oxygen bond, the hydroperoxide **9** reacts with another molecule **2** to produce a hydroxyl radical, an enol complex **10** as well as a phosphite radical **5**. The enolate **10** quickly undergoes tautomerization to its keto form **3**. Meanwhile, the hydroxyl radical produced further reacts with $(RO)_2P(O)H$ **2** to give another phosphite radical **5** (Scheme 2-II). Dialkyl phosphate **11** is formed via termination reaction of hydroxyl radical and phosphite radical **5** in the reaction process (Scheme 2-III). ^{31}P NMR traced the progress of the reactions. Besides the main product **3a**, the ^{31}P NMR stacks diagram shown in Figure 1 proved the formation of dialkyl phosphate **11a**. In addition, ^{31}P NMR stacks diagram didn't offer support for the formation of alkynlphosphates in the reaction process. ^{31}P NMR signal from alkynylphosphate should appear at around -5 ppm.[14] But no trace of such a signal was detected by ^{31}P NMR. Zhao' group has reported that copper-catalyzed aerbic oxidative coupling of terminal alkynes with H-phosphonates can lead to the formation of alknylphosphonates in high yield.[14] However, with the same materials, alknylphosphonates were not detected under our different reaction conditions, implying that the target products, β-ketophosphonates, were not possibly formed via the hydration of alkynylphophonates in our cases. It is quite understandable, because we have already known that this one-pot reaction proceeds via a radical chain mechanism. The mechanism proposed in Scheme 2 dose not support the formation of alkynylphosphate in the reaction process. The last strong support for our proposed mechaniem is from the formation of product **3aa**, which was synthesized starting from 1-phenyl-1-propyne, an internal aromatic alkyne. It is clear that it is only terminal alkynes that can react with *H*-phosphonates via an aerobic oxidative coupling reaction to generate alkynylphosphonates.[14] The formation of **3aa** here once again offers support for the radical mechanism shown in Scheme 2 and excludes the possibility of formation of β-ketophosphonates via a hydration of alkynylphosphate.

Conclusions

In conclusion, we have developed a straightforward method by which a wide variety of β-ketophosphonates were prepared in a one-pot aerobic reaction of alkynes with dialkyl *H*-phosphonates in the presence of silver/copper catalysts and $K_2S_2O_8$ at room temperature within 3 h. The current substrate scope encompasses a series of alkynes, including aromatic alkynes, aliphatic alkynes, as well as a series of organophosphorous reagents, including

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diphenylphosphine oxide and ethyl phenylphosphinate, and dialkyl *H*-phosphonates. To the best of our knowledge, this reaction is the first example using easily available silver/copper/$K_2S_2O_8$ catalytic system to perform the oxyphosphorylation reaction. Compared with literature methods, great advantages of this strategy include high efficiency, readily available catalysts and starting materials, time-saving one-pot procedure, and extremely mild and open air conditions. The method will undoubtedly be a far superior alternative for the synthesis of a variety biologically and chemically significant β-ketophosphonates. Further studies on the applications of this strategy will be reported in due course.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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