Copper-Catalyzed Aerobic Oxidative/Decarboxylative Phosphorylation of Aryl Acrylic Acids with P(III)-Nucleophiles

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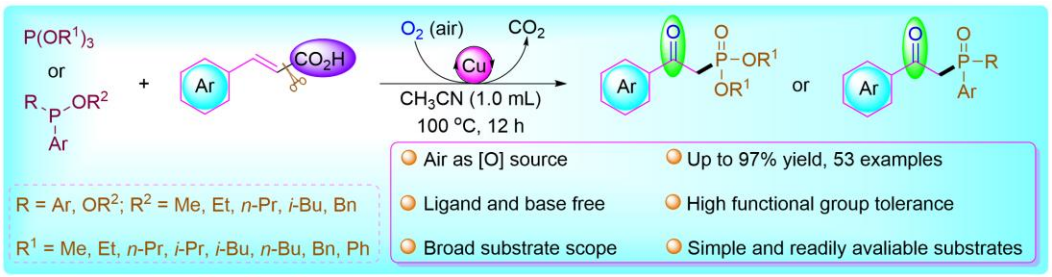
Abstract



A copper-catalyzed aerobic oxidative/decarboxylative phosphorylation of aryl acrylic acids with P(III)-nucleophiles *via* the Michaelis-Arbuzov rearrangement for the synthesis of *β*-ketophosphine oxides, *β*-ketophosphinates and *β*-ketophosphonates is reported. The present reaction could be conducted effectively without the use of ligand and base. Various kinds of aryl acrylic acids and P(III)-nucleophiles are tolerated in the transformation, generating the desired *β*-keto-organophosphorus compounds as a valuable class of phosphorus-containing intermediates with good to excellent yields. In addition, the possible mechanism and kinetic study for the reaction have been explored by step-by-step control experiments and competitive experiments, and the results proved that this transformation may follow a second-order manner in chemical kinetics, as well as a radical process, respectively.

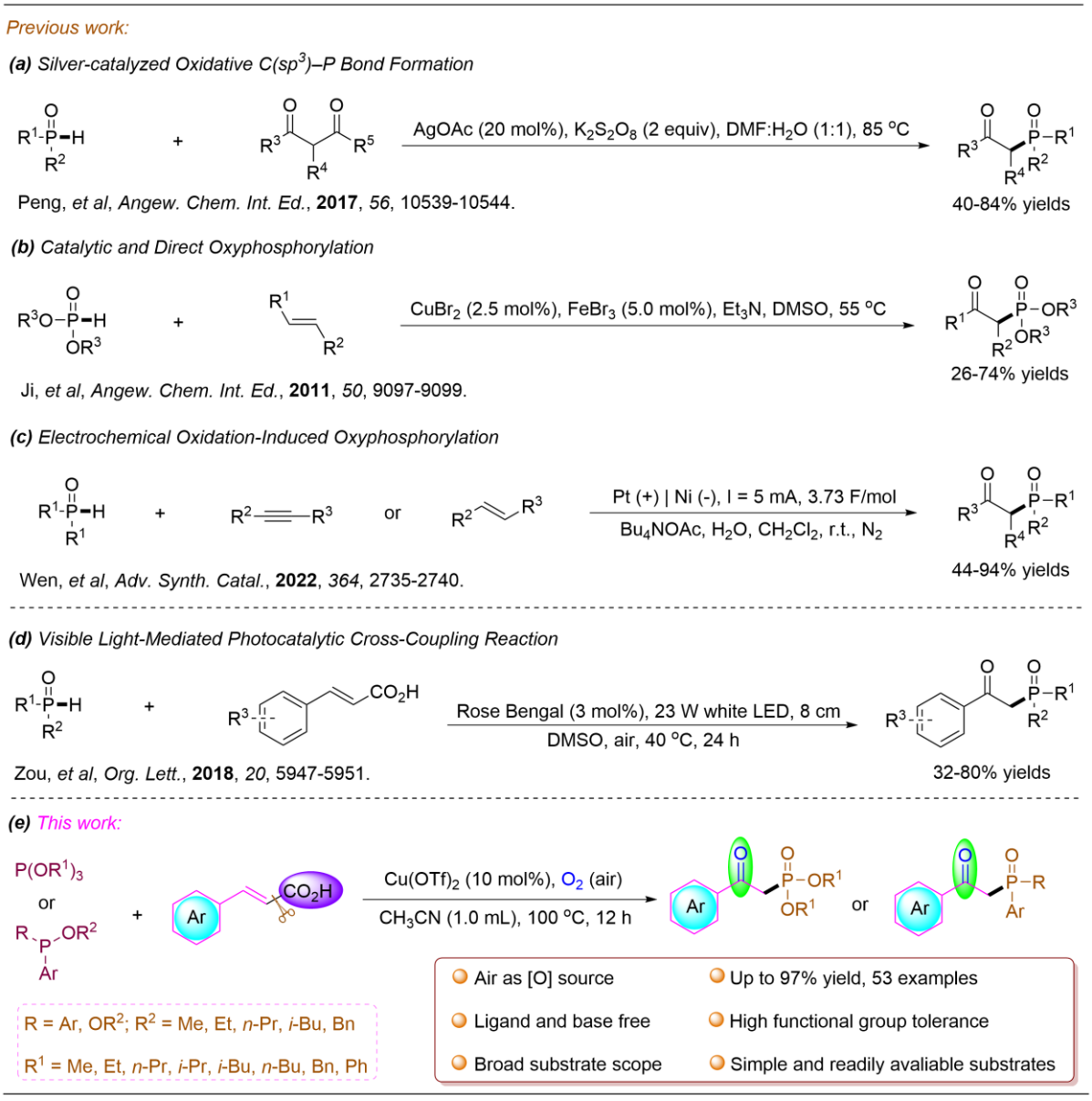
Introduction

Phosphorus-containing compounds constitute the versatile structure in organic and medicinal chemistry.[1] Amongst these, *β*-ketophosphine oxides are recognized as one of the most privileged motifs, which are applied in various kinds of fields, such as building blocks for the synthesis of various high value-added chemicals and drug-like molecules,[2] extractants for metal ions[3] and potential ligands for organic synthesis[4] due to their coordination ability. In addition, they are endowed with outstanding biological properties in treating diarrhea and skin infection caused by bacterial infection.[5] In view of the importance of these compounds, it is an important subject to develop green and efficient synthetic methods to access such kinds of structures.

Traditionally, *β*-ketophosphinates can be synthesized by the Michaelis-Arbuzov reaction of α-haloketones with trialkylphosphites,[6] which are a milestone in organophosphorus chemistry developed over 100 years and has been widely used to synthesize various kinds of organic phosphorus compounds. However, toxic alkyl halides are usually used as the raw materials in this classical transformation, and it is unavoidable to produce low boiling ethyl halides as the byproduct, which will lead to side reactions, lowering the atomic efficiency and causing related environmental problems.[7]

Another efficient method for the synthesis of *β*-keto-organophosphorus compounds is *via* the acylation of alkylphosphine oxides.[8] For example, Peng *et al*. in 2017 disclosed a silver-catalyzed oxidative C(sp^3)−H/P−H cross-coupling of 1,3-dicarbonyl compounds with *H*-phosphonates, and tandem exclusive C(sp^3)−C(CO) bond cleavage, generating the desired *β*-ketophosphonates with good yields (**Scheme 1a**).[9]

Scheme 1. Representative approaches for the synthesis of *β*-keto-organophosphorus compounds.



Recently, some elegant reports to acess *β*-ketophosphonates have been described based on the transition-metal catalyzed oxyphosphorylation of alkenes and their derivatives.[10] For instance, Ji *et al*. proposed an efficient method to build *β*-ketophosphonates *via* the transition-metal catalyzed oxyphosphorylation of alkenes with dioxygen and *H*-phosphonates (**Scheme 1b**).[11] In 2022, Wen and coworkers reported a metal- and exogenous-oxidant-free oxidation-induced oxyphosphorylation of hydrocarbon with water for the generation of *β*-ketophosphonates (**Scheme 1c**).[12]

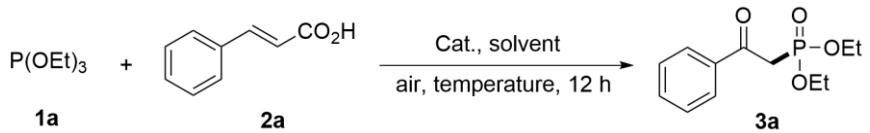
On the other hand, aryl acrylic acids are one of the most versatile starting materials in the transition metal-catalyzed decarboxylation cross-coupling reactions, which can be efficiently used as the precursor to construct C−C,[13] C−N,[14] C−S[15] and C−P[16] bonds because of their commercial availability and structural diversity. In recent years, there have been increasing reports on the synthesis of β-ketophosphonates using *H*-phosphonates, which are P(V)-nucleophiles, as phosphorylation reagents. For instance, Song *et al.* demonstrated the formation of β-ketophosphonates through a Cu/Fe-cocatalyzed domino Knoevenagel–decarboxylation–oxyphosphorylation sequence from aromatic aldehydes and *H*-phosphonates.[16b] They also achieved deesterification of cinnamyl/alkynyl carboxylates with *H*-phosphonates.[16c] Similarly, Chen *et al.* developed a protocol that allows for the creation of β-ketophosphonates by reacting alkenyl acids or alkenes with H-phosphonates and oxygen, catalyzed by $CuSO_4 \cdot 5H_2O$.[16h] Meanwhile, photocatalytic reaction is widely used in the synthesis of organophosphorus.[17] In 2018, Zou *et al*. reported a visible light-mediated decarboxylative oxyphosphorylation of cinnamic acids with diarylphosphine oxides using Rose Bengal as the photocatalyst (**Scheme 1d**).[18] It can be seen that the aforementioned synthetic methods mainly started from P(V)-H compounds. Owing to the fact that P(V)-H nucleophiles are obtained through the hydrolysis of P(III)-Cl derivatives, environmental pollution and energy consumption inevitably occurred in the process of transformation. Therefore, considering the cost and accessibility of P(III) compounds, the use of P(III) nucleophiles as the phosphorus source to synthesize *β*-ketophosphine oxides, *β*-ketophosphinates and *β*-ketophosphonates is of great advantages. Herein, with our continuous development of efficient synthetic methods for organophosphorus compounds,[19] we reported a copper-

catalyzed aerobic oxidative/decarboxylative phosphorylation of cinnamic acids with P(III)-nucleophiles leading to *β*-ketophosphine oxides, *β*-ketophosphinates and *β*-ketophosphonates by using air as the oxygen source (**Scheme 1e**).

Results and discussion

Initially, we wish to use P(III)-nucleophiles as the phosphorylation reagents to undergo the decarboxylative coupling reaction with cinnamic acids under the action of water for generating new C-P bond. To test our conjecture, triethylphosphite (**1a**) and cinnamic acid (**2a**) were selected as the model substrates to optimize the reaction conditions (**Table 1**). At the outset of our investigation, different kinds of Lewis catalysts, such as $FeCl_3$, $ZnBr_2$, $AgNO_3$, CuI, $Cu(OAc)_2$, $Cu(OTf)_2$, $CuCl_2$, $CuBr_2$, and $Cu(NO_3)_2$ were investigated (**Table 1**, entries 1-9). Gratifyingly, when $Cu(OTf)_2$ was added to the reaction as the catalyst, the desired product **3a** was generated with the yield of 91% in acetonitrile at 100 °C (**Table 1**, entries 6). For further optimization, other solvents such as toluene, acetone, 1,4-dioxane, DMF, DMSO, THF and DCM were subjected to the reactions instead of CH_3CN (**Table 1**, entries 10-16). However, these reaction media failed to promote the reaction well and even restrained the reaction, indicating that the solvent CH_3CN played a vital role for the transformation. With these results in hand, we further explored the influences of the catalyst loading for the reaction (**Table 1**, entries 17-20). It is apparent that the reaction proceeded with the highest yield when 10 mol% amount of $Cu(OTf)_2$ was employed as the catalyst. With the increase of the reaction temperature from 25 to 100 ºC, the yield of the desired product **3a** was greatly improved (**Table 1**, entry 6 and entries 21-24). When the reaction temperature was increased from 100 to 120 ºC, the yield of **3a** decreased probably due to the side reaction or the hydrolysis of **1a** (**Table 1**, entry 25). In addition, it was observed that the desired product **3a** can hardly be generated when the reaction was operated under nitrogen atmosphere, indicating that the oxygen might be involved in the oxidative process (**Table 1**, entry 26). Based on the above optimization results, the optimal reaction conditions are as follows: $Cu(OTf)_2$ (10 mol%), 100 ºC, CH_3CN (1.0 mL), air atmosphere (**Table 1**, entry 6).

Table 1. Optimization of the reaction conditions. [a]



1a **2a** **3a**

Entry	Catalyst (mol%)	Solvent (1 mL)	Temp. (°C)	Yield [b]
1	$FeCl_3$ (10)	CH_3CN	100	ND
2	$ZnBr_2$ (10)	CH_3CN	100	ND
3	$AgNO_3$ (10)	CH_3CN	100	30%
4	CuI (10)	CH_3CN	100	ND
5	$Cu(OAc)_2$ (10)	CH_3CN	100	32%
6	**$Cu(OTf)_2$ (10)**	**CH_3CN**	**100**	**91% (88%)**
7	$CuCl_2$ (10)	CH_3CN	100	35%
8	$CuBr_2$ (10)	CH_3CN	100	42%
9	$Cu(NO_3)_2$ (10)	CH_3CN	100	32%
10	$Cu(OTf)_2$ (10)	$PhCH_3$	100	39%
11	$Cu(OTf)_2$ (10)	Acetone	100	17%
12	$Cu(OTf)_2$ (10)	1,4-Dioxane	100	42%
13	$Cu(OTf)_2$ (10)	DMF	100	65%
14	$Cu(OTf)_2$ (10)	DMSO	100	49%
15	$Cu(OTf)_2$ (10)	THF	100	22%
16	$Cu(OTf)_2$ (10)	DCM	100	37%
17	$Cu(OTf)_2$ (0)	CH_3CN	100	ND
18	$Cu(OTf)_2$ (1)	CH_3CN	100	ND
19	$Cu(OTf)_2$ (5)	CH_3CN	100	56%
20	$Cu(OTf)_2$ (20)	CH_3CN	100	88%
21	$Cu(OTf)_2$ (10)	CH_3CN	25	ND
22	$Cu(OTf)_2$ (10)	CH_3CN	40	11%
23	$Cu(OTf)_2$ (10)	CH_3CN	60	36%
24	$Cu(OTf)_2$ (10)	CH_3CN	80	76%
25	$Cu(OTf)_2$ (10)	CH_3CN	120	80%
26	$Cu(OTf)_2$ (10)	CH_3CN	100	ND [c]

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), catalyst and solvent (1.0 mL) at the indicated temperature for 12 h under air. [b] Yield was determined by GC analysis, using dodecane as the internal standard. The value in parentheses is the isolated yield. [c] The reaction was conducted under nitrogen.

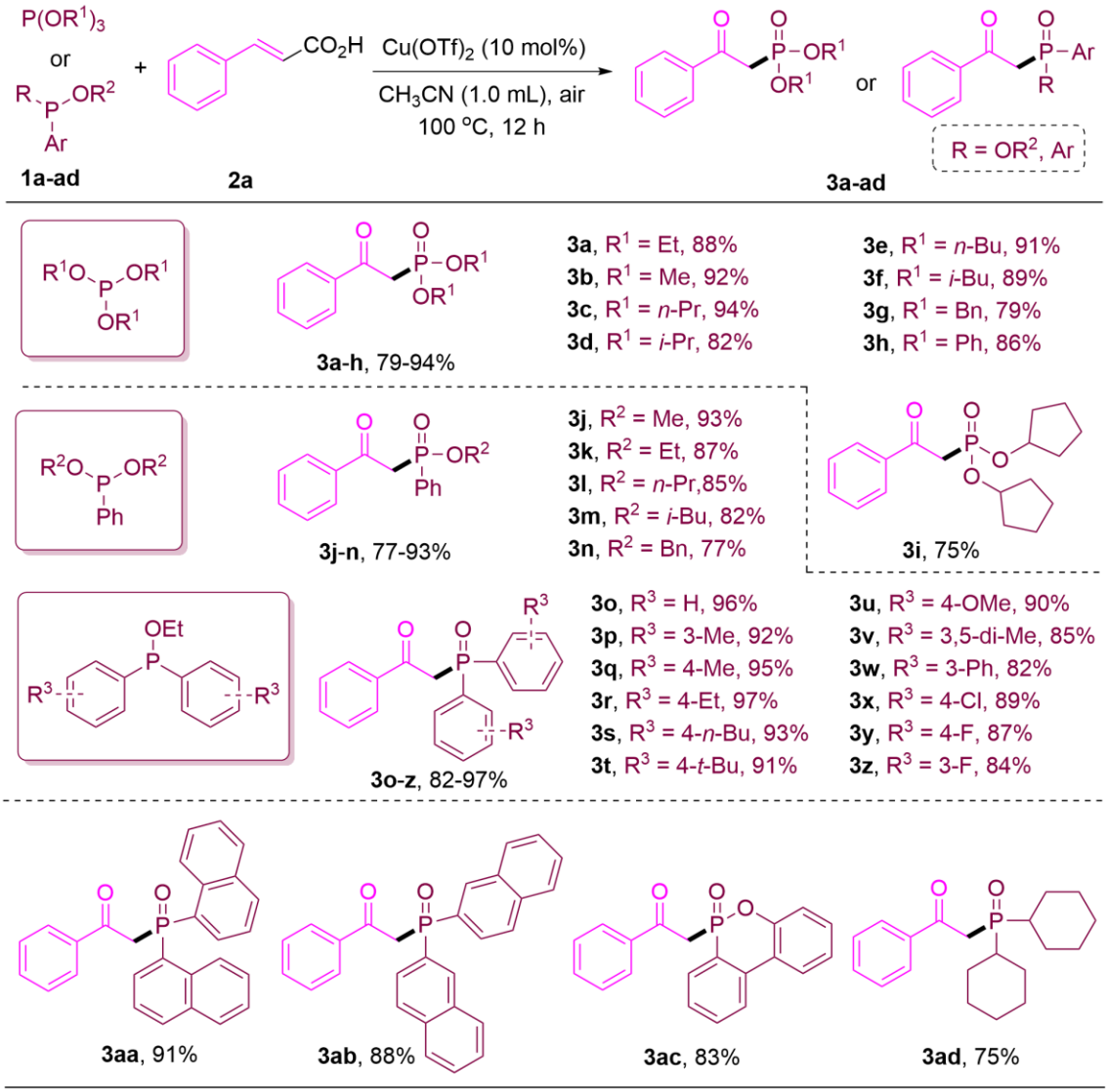
With the optimized results in hand, the substrate scope of cinnamic acid (**2a**) with P(III)-nucleophiles was examined under the standard conditions (**Scheme 2**). To our delight, when phosphites bearing different alkyl groups, such as ethyl (**1a**), methyl (**1b**) and *n*-propyl (**1c**), *iso*-propyl (**1d**), *n*-butyl (**1e**), *iso*-butyl (**1f**) and benzyl (**1g**) were employed as the substrates, the corresponding dialkyl (2-*oxo*-2-

phenylethyl)phosphonates **3a**-**g** could be synthesized in 79-94% yields. When triphenylphosphite (**1h**) was selected as the substrate to react with **2a**, the reaction can proceed smoothly to deliver **3h** in 86% yield. In addition, tricyclopentylphosphite (**1i**) was also found tolerable in this transformation, and the desired product **3i** could be obtained in 75% yield. Encouraged by the reaction of triphenylphosphite (**1h**) with **2a**, we further investigated the substrate scope regarding phosphonites containing different aryl and alkoxy groups. It is found that dimethylphenylphosphonite (**1j**), diethylphenylphosphonite (**1k**), dipropylphenylphosphonite (**1l**), diisobutylphenylphosphonite (**1m**) and dibenzylphenylphosphonite (**1n**) could be used in the aerobic oxidative/decarboxylative phosphorylation transformation to generate the expected target products **3j**-**n** in 77-93% isolated yields. In order to further investigate the reactivity of P(III)-phosphites, ethoxydiphenylphosphane (**1o**) was chosen as the substrate to react with cinnamic acid **2a**, and the corresponding product **3o** can be synthesized in 96% yield as expected. Additionally, it is clear that a series of ethoxydiarylphosphanes bearing electron-donating groups, such as ethoxydi-*m*-tolylphosphane (**1p**), ethoxydi-*p*-tolylphosphane (**1q**), ethoxybis(4-ethylphenyl)phosphane (**1r**), bis(4-butylphenyl)(ethoxy)phosphane (**1s**), bis(4-(*tert*-butyl)phenyl)(ethoxy)phosphane (**1t**), ethoxybis(4-methoxyphenyl)phosphane (**1u**), bis(3,5- dimethylphenyl)(ethoxy)phosphane (**1v**) and di([1,1'-biphenyl]-3-yl)(ethoxy)phosphane (**1w**) exhibited high reactivity toward cinnamic acid (**2a**), delivering the corresponding phosphorylation products **3p-w** in 82-97% yields.

On the other hand, when ethoxydiarylphosphanes containing different electron-withdrawing substituents (**1x-1z**) on the aryl ring were selected as the starting materials for the reaction, the corresponding products 2-(bis(4-chlorophenyl)phosphoryl)-1-phenylethan-1-one (**3x**), 2-(bis(4-fluorophenyl)phosphoryl)-1-phenylethan-1-one (**3y**) and 2-(bis(3-fluorophenyl)phosphoryl)-1-phenylethan-1-one (**3z**) were obtained in 84-89% isolated yields. Furthermore, 2-(di(naphthalen-1-yl)phosphoryl)-1-phenylethanone (**3aa**) and 2-(di(naphthalen-2-yl)phosphoryl)-1-phenylethanone (**3ab**) could be synthesized in 91% and 88% yields through the reactions of ethoxydi(naphthalen-1-yl)phosphane (**1aa**) and ethoxydi(naphthalen-2-yl)phosphane (**1ab**) with **2a**, respectively. When 6-ethoxy-6*H*-dibenzo[*c*,*e*][1,2]oxaphosphinine (**1ac**) was adopted as the substrate to react with **2a**, the

desired product **3ac** could be obtained in 83% yield. To our delight, 2-(dicyclohexylphosphoryl)-1-phenylethan-1-one (**3ad**) was obtained in 75% yield *via* the Cu-catalyzed aerobic axidative/decarboxylative phosphorylation reaction of cinnamic acid (**2a**) with **1ad** under the standard conditions. Meanwhile, the configuration of **3v** was unambiguously determined by X-ray single crystal diffraction analysis (**Figure 1**).

Scheme 2. Substrate scope of P(III)-phosphites. [a]



[a] Reaction conditions: P(III)-nucleophiles (**1a-ad**, 0.2 mmol), cinnamic acid (**2a,** 0.2 mmol), $Cu(OTf)_2$ (10 mol%), CH_3CN (1.0 mL), air, 100 °C, 12 h. Isolated yields.

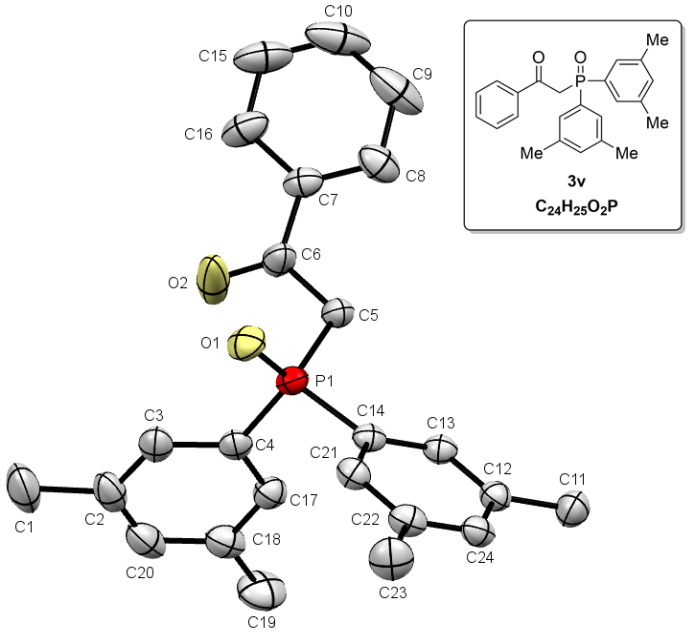
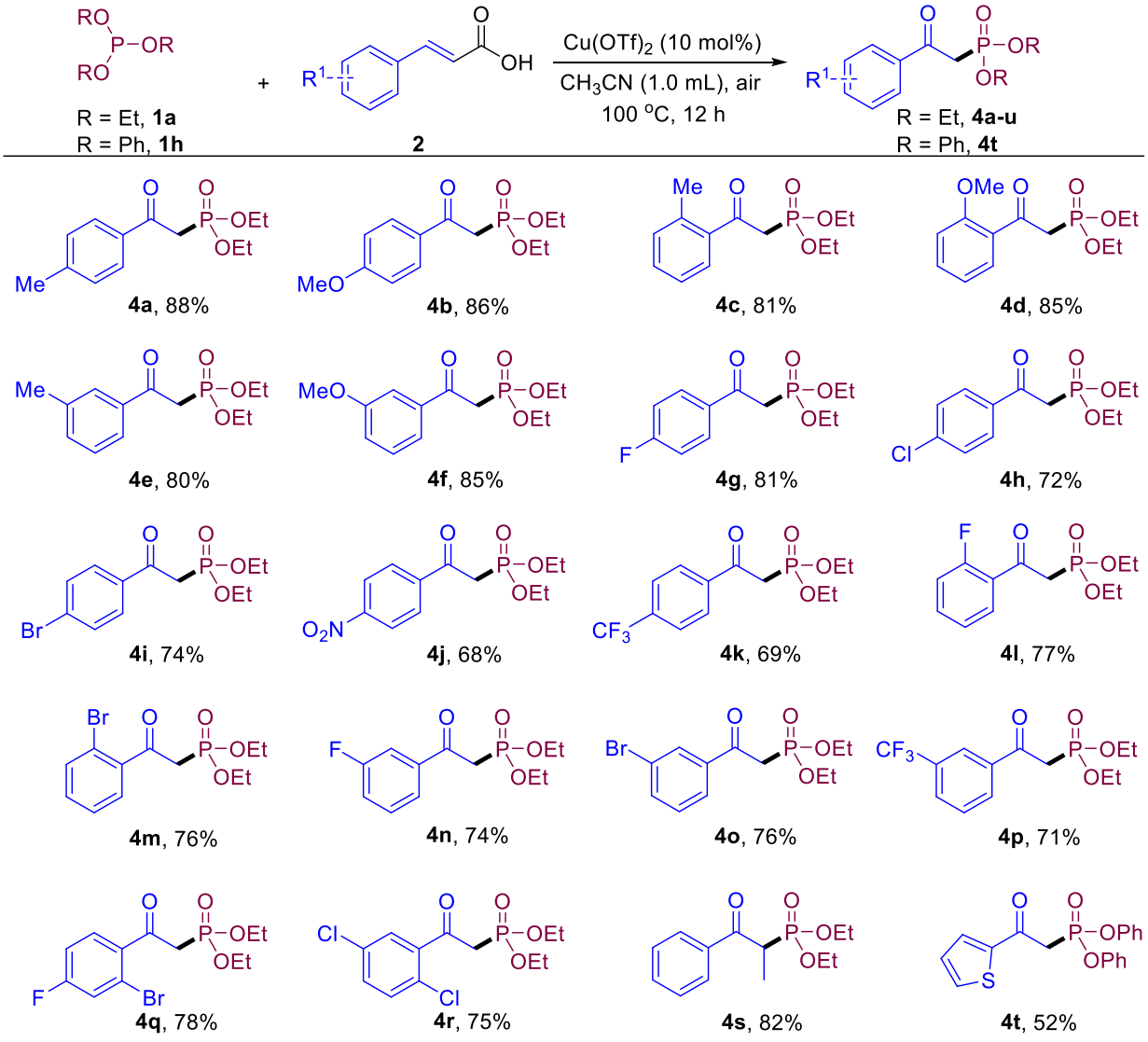


Figure 1. ORTEP drawing of compound **3v**.[20] Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: O2-C6 1.204(3), C5-C6 1.514(3), P1-C5 1.817(2), P1-O1 1.486(16), P1-C4 1.803(2), P1-C14 1.807(2); O2-C6-C7 119.8(2), O2-C6-C5 120.4(2), C6-C5-P1 111.45(14), O1-P1-C5 113.35(9), O1-P1-C4 112.75(10), O1-P1-C14 111.35(10).

As depicted in **Scheme 3**, the copper-catalyzed aerobic oxidative/decarboxylative/phosphorylation reaction of triethyl phosphite (**1a**) with cinnamic acid (**2a**) leading to diethyl (2-oxo-2-phenylethyl)phosphonate (**3a**) can be applied to different kinds of aryl acrylic acids. It is clear that the aryl moiety in aryl acrylic acids containing different electron-donating groups, such as 4-methyl (**2b**), 4-methoxy (**2c**), 2-methyl (**2d**), 2-methoxy (**2e**), 3-methyl (**2f**) and 3-methoxy (**2g**), can react with triethylphosphite (**1a**) effectively to afford the desired products **4a**-**f** in 80-88% yields under the optimized reaction conditions. In addition, when the aryl ring of aryl acrylic acids substituted with electron-withdrawing groups (*e.g.* 4-F, 4-Cl, 4-Br, 4-NO_2, 4-CF_3, 2-F, 2-Br, 3-F, 3-Br, 3-CF_3, 2-Br-4-F and 2,5-*di*-Cl, **2h**-**s**) were selected as the substrates to react with **1a**, the corresponding diethyl (2-oxo-2-arylethyl)phosphonates **4g**-**r** could be synthesized in 68-81% yields. Furthermore, the α-substituted 2-methyl-3-phenylacrylic acid **2t** also showed positive result toward the reaction, and the expected product diethyl (1-oxo-1-phenylpropan-2-yl)phosphonate (**4s**) was formed with 82% yield. In addition,

it is worth noting that 3-(thiophen-2-yl)acrylic acid showed positive result for the reaction, which could react with triphenylphosphite (**1h**) efficiently to generate the target compound **4t** in 52% yield under the present reaction conditions. These results further demonstrated the suitability of the aryl acrylic acids in this transformation.

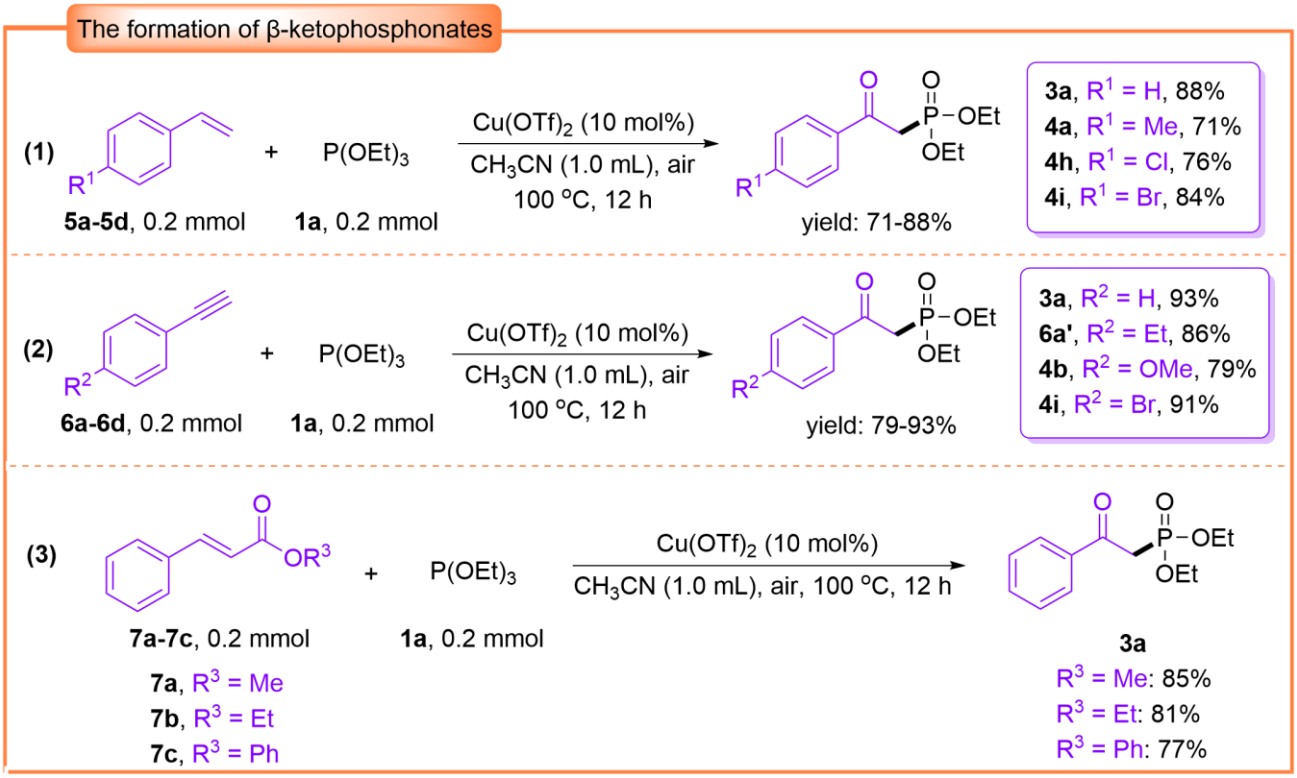
Scheme 3. Substrate scope of aryl acrylic acids.[a]



[a] Reaction conditions: triethylphosphite or triphenyl phosphite (0.2 mmol), cinnamic acid derivatives (**2**, 0.2 mmol), $Cu(OTf)_2$ (10 mol%), CH_3CN (1.0 mL), air, 100 °C, 12 h. Isolated yields.

To better demonstrate the generality of this method, styrene and alkyne derivatives were selected as the starting materials to react with triethylphosphite (**1a**) under the standard conditions (**Scheme 4**). Initially, styrene and its derivatives with different substituents (*e.g.* 4-Me, 4-Cl and 4-Br) (**5a-d**) were employed as substrates to react with **1a** *via* Cu(II) catalysis, the corresponding products (**3a**, **4a**, **4h** and **4i**) were generated in 71-88% yields. Subsequently, the copper-catalyzed direct oxyphosphorylation of the alkynes derivatives **6a-d** with **1a** could proceed smoothly with the oxyphosphorylation products (**3a**, **6a′**, **4b** and **4i**) obtained in 79-93% yields. Besides these transformations, this method was also found applicable in the deesterification and oxyphosphorylation reaction of cinnamates (**7a-c**) with **1a**, and the expected product **3a** could be generated in the range of 77-85% yields according to the different substitutent in cinnamates.

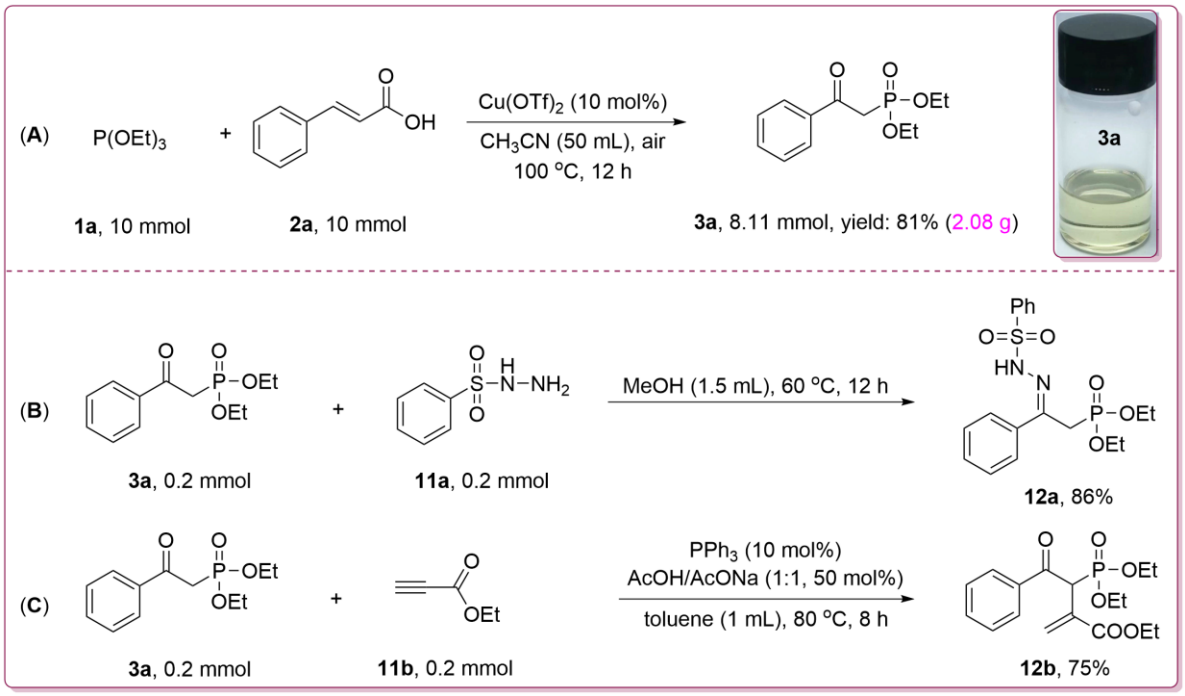
Scheme 4. Different routes to access diethyl (2-*oxo*-2-arylethyl)phosphonates.



Under the optimized reaction conditions, a gram-scale synthesis of **3a** was conducted through the reaction of triethylphosphite (**1a**) with cinnamic acid (**2a**) (**Scheme 5A**). After simple purification, the

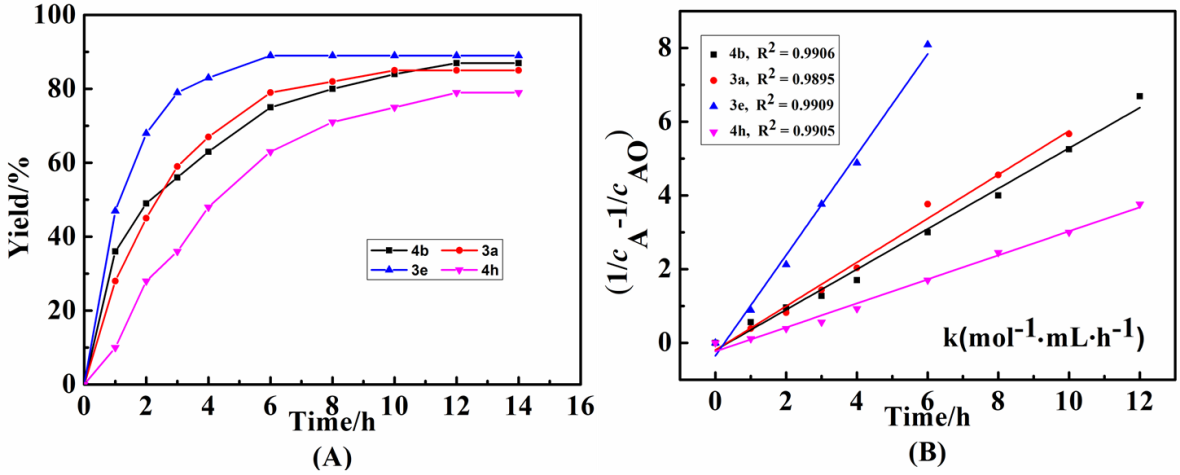
target product **3a** was generated with 81% yield (2.08 g), satisfying the practical application requirements. It is worth pointing out that the carbonyl group and methylene group in **3a** is of good modifiability according to its specific molecular structure. Therefore, a series of selective functionalization experiments for **3a** were designed. For example, in protonic solvent, the carbonyl group of **3a** could react with benzenesulfonohydrazide (**11a**) to generate (*E*)-diethyl (2-phenyl-2-(2-(phenylsulfonyl)hydrazono)ethyl)phosphonate (**12a**) in 86% yield (**Scheme 5, path B**),[21] which can be efficiently converted into organophosphorus compounds with high added value selectively. In addition, ethyl 3-(diethoxyphosphoryl)-2-methylene-4-oxo-4-phenylbutanoate (**12b**) can also be synthesized in 75% yield through the Michael-type addition of the methylene substituent in **3a** to ethyl propiolate (**11b**) by PPh_3 catalysis (**Scheme 5, path C**).[22]

Scheme 5. Large-scale synthesis and selective functionalization of **3a**.



In order to understand the reaction from dynamics side, as monitored by GC and ^{31}P NMR analysis, a series of tracking experiments were conducted under the optimized reaction conditions to confirm the reaction order of this transformation (**Figure 2**).[23] The experimental results show that whether the aryl

acrylic acid or the P(III)-nucleophile is used as the key factor, the concentration of the substrate in the reaction system follows a second-order dependence ($(1/C_A-1/C_{A0})=k't$), which means that the intermolecular catalysis is involved in this transformation, and the substrate is effectively activated through the double activation process. R^2 is the correlation coefficient of the linear equation. The closer the calculated correlation coefficient is to 1, the more accurate the fitted linear equation is.



(1) Reaction impedance rate equation: $-r_A = kC_AC_B$

$$-\frac{dC_A}{dt} = C_{A0}\frac{dx_A}{dt} = kC_{A0}(1-x_A)(C_{B0}-C_{A0}x_A)$$

(2) Initial concentration ratio: $M = \frac{C_{B0}}{C_{A0}}$

$$\int_0^{x_A}\frac{dx_A}{(1-x_A)(M-x_A)} = kC_{A0}\int_0^t dt$$

(3) The initial concentration ratio satisfies : $C_{A0} = C_{B0}$, so, $M = 1$

(4) The above formula can be transformed into: $\left(\frac{1}{C_A}-\frac{1}{C_{A0}}\right) = k't$

Figure 2. (A): Reaction yields of **4b**, **3a**, **3e** and **4h** versus the reaction time. (B): the fitting line of reaction order expressed by the relationship between $(1/C_A-1/C_{A0})$ and time.

In addition, to further explore the preliminary mechanism of this reaction, we carried out Hammett analysis on aryl acrylic acids (**2a**, **2b**, **2c**, **2h**, **2j** and **2l**) and P(III)-nucleophiles (**1o**, **1q**, **1t**, **1u**, **1x** and **1y**), respectively. As shown in **Figure 3**, a large negative slope was determined for the reaction of *para*-substituted diarylethylphosphites with cinnamic acid (**2a**) (ρ = -1.63). This large negative ρ constant indicates the decrease of electron density resulted in the decrease of free radical reaction activity of

P(III)-phosphites, which is consistent with the Michaelis-Arbuzov rearrangement as a rate-determining step. Meanwhile, for the reaction of *para*-substituted cinnamic acids with triethylphosphite (**1a**), a negative slope (ρ = -0.97) was observed. The results indicated that the electron-donating groups on the aryl ring contributed to the electron density of unsaturated double bond of cinnamic acids, which urged cinnamic acids more susceptible to the attack by the oxygen radical.[24]

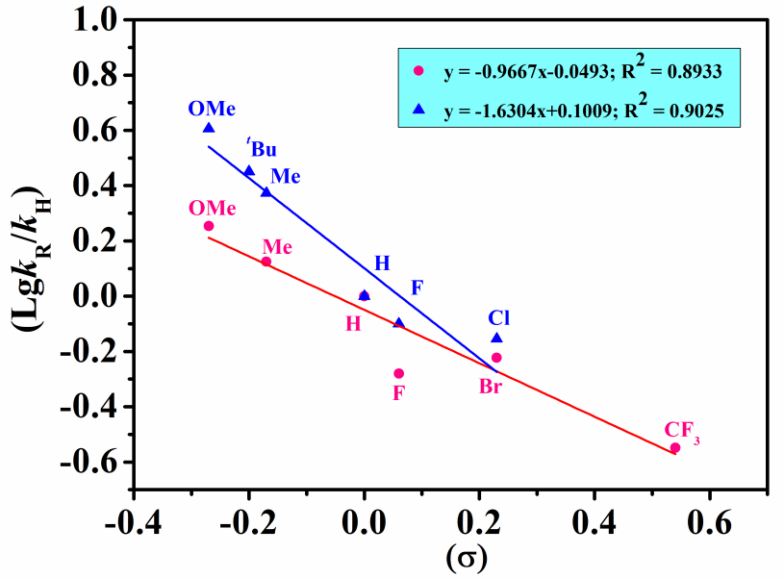
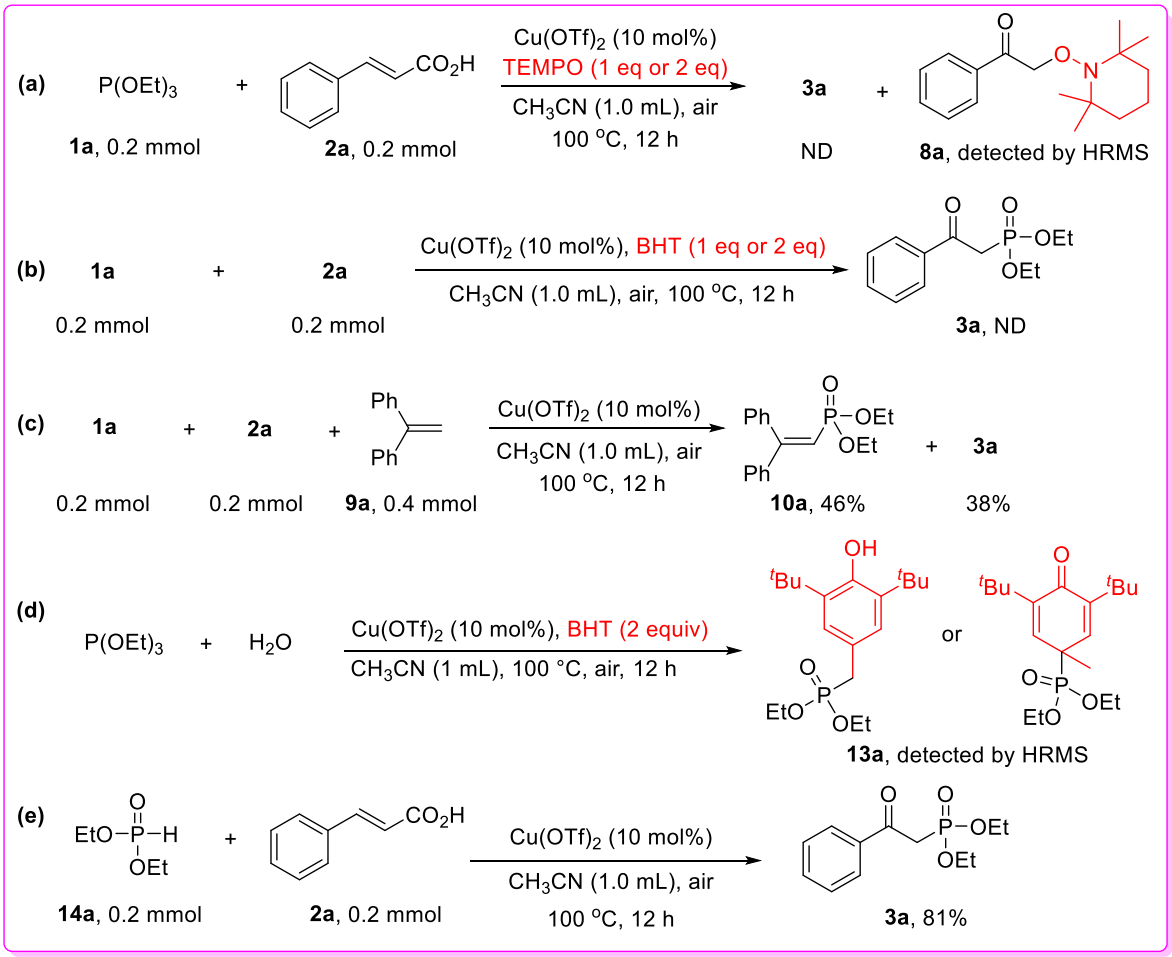


Figure 3. Investigation of Hammett effects. Blue: the effect of *para*-substitution on diarylethylphosphites. Red: the effect of *para*-substitution on cinnamic acids.

With these results in hand, a series of control experiments were carried out under the standard condition to further understand the reaction mechanism (**Scheme 6**). Initially, we conducted the reaction of triethylphosphite (**1a**) with cinnamic acid (**2a**) under the standard reaction conditions with the addition of 2,2,6,6-tetramethylpiperidine N-oxyl (TEMPO, 1.0 eq or 2.0 eq.) or 2,6-di-*tert*-butyl-4-methylphenol radical (BHT, 1.0 eq or 2.0 eq.) as the radical scavenger, as monitored by high resolution mass spectrum (HRMS) and ^{31}P NMR analysis, the desired product **3a** can hardly be formed during the reaction (**Scheme 6a** and **6b**). As detected by GC-MS (**Figure S1**) and HRMS (**Figure S2**), a possible radical segment **8a** was observed (**Scheme 6a**), which indicates that the reaction may proceed *via* a radical process, and the proposed acyl radical intermediate is produced *in-situ* during the reaction. In

addition, when ethene-1,1-diyldibenzene (**9a**) was added to the reaction as a free radical trapping agent, the desired product was obtained in 38% yield, and **9a** was converted to **10a** in 46% yield (**Scheme 6c**). Furthermore, when triethylphosphite was used as the starting material to react with H_2O under the present reaction conditions with the addition of 2 equivalents BHT as the radical scavenger, the possible radical adduct **13a** was observed by HRMS analysis (**Figure S3**), indicating that a $(EtO)_2P(O)$• radical may be produced *in-situ* during the reaction (**Scheme 6d**).[25] In order to verify whether the P(O)-H compound can react with **2a** under the present reaction conditions, diethyl phosphonate (**14a**) was selected as the phosphorylation substrate for this transformation, and the corresponding product **3a** could be synthesized in 81% yield (**Scheme 6e**), indicating that diethyl phosphonate might be a possible intermediate.

Scheme 6. Control experiments.

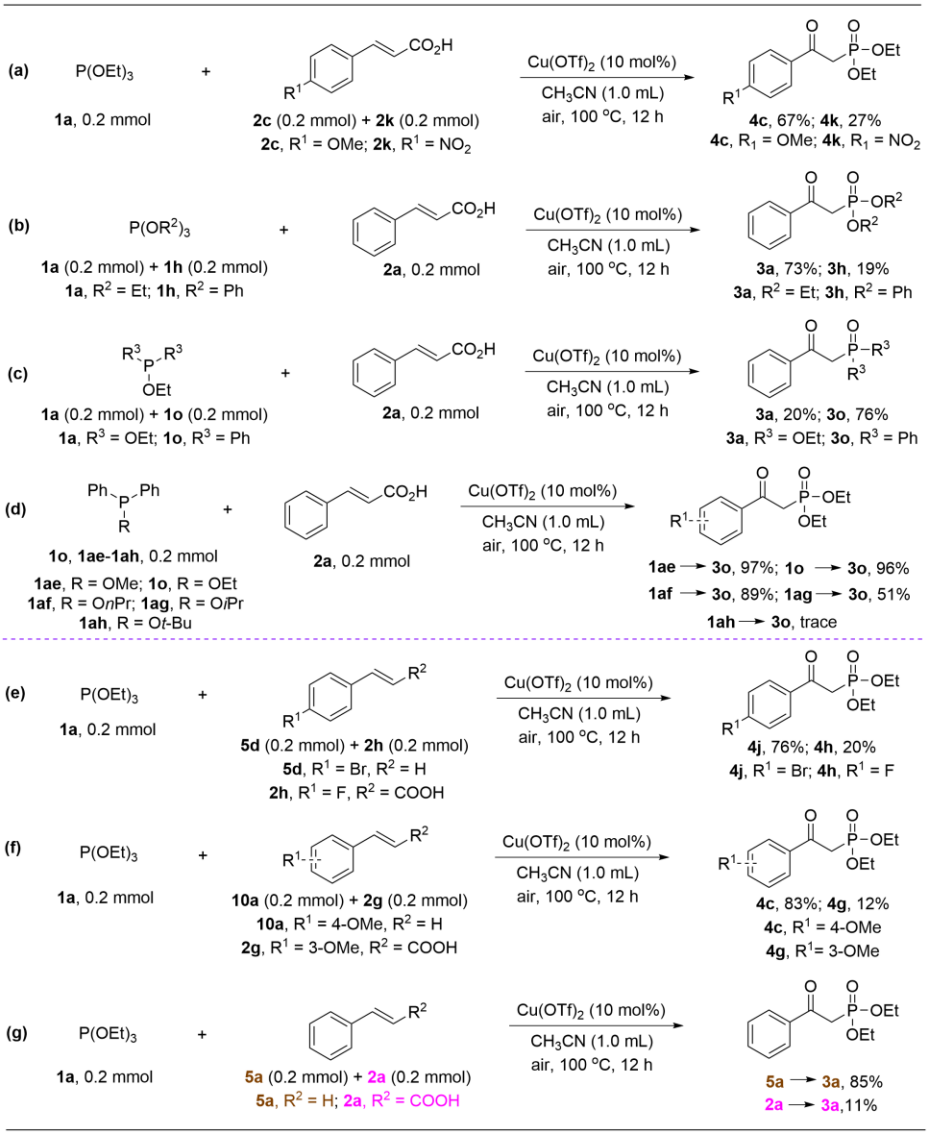


Furthermore, a range of competitive reactions were explored under the standard conditions. For example, as shown in **Scheme 7a**, when aryl acrylic acids bearing groups with different electron properties, such as, **2c** (4-OMe) and **2k** (4-NO_2) are used as the substrates to react with triethylphosphite **(1a)** simultaneously, as confirmed by GC and ^{1}H NMR analysis, the products **4c** and **4k** could be synthesized in 67% and 27% yield, respectively. Subsequently, when different phosphites, such as, **1a** ($P(OEt)_3$) and **1h** ($P(OPh)_3$) are adopted as the substrates to react with cinnamic acid (**2a**) in a one-pot reaction under the standard conditions (**Scheme 7b**), the result showed that **1a** has a higher reactivity than **1h** during the reaction. Moreover, we further investigated the effect of substituents on the phosphorus atom center using triethylphosphite (**1a**) and ethoxydiphenylphosphine (**1o**) as the competitive raw materials. Because **1o** contains two phenyl substituents, which leads to the low electron cloud density of its phosphorus atom center, the P-OEt bond of **1o** is easier to leave than that of **1a**. Therefore, after the reaction, the yields of **3a** and **3o** were 20% and 76%, respectively (**Scheme 7c**). Meanwhile, alkoxydiphenylphosphines with different substituents such as methoxydiphenylphosphane (**1ae**), ethoxydiphenylphosphane (**1o**), diphenyl(propoxy)phosphane (**1af**), isopropoxydiphenylphosphane (**1ag**), *tert*-butoxydiphenylphosphane (**1ah**) were subjected to react with cinnamic acid (**2a**) under the standard condition respectively. As shown in **Scheme 7d**, with the increase of steric hindrance of substituents, the yields of expected target products decrease gradually, indicating the steric hindrance influence on P(III)-nucleophiles in the reaction. As shown in **Scheme 7e-g**, to verify and compare the reactivity of alkenes (**5a**, **5d**, **11a**) and aryl acrylic acids (**2a**, **2h**, **2g**), a series of competitive experiments were performed. which suggested that the alkenes showed better reactivity than aryl acrylic acids in this transformation.

On the basis of the above experimental results and reported literatures,[26] a plausible mechanism for the aerobic oxidative/decarboxylative phosphorylation reaction is described as shown in **Scheme 8 (path I)**. Firstly, the solvent CH_3CN coordinates with copper (II) ion to form acetonitrile-soluble complex $[Cu(MeCN)_n]^{2+}$ (**A**) to initiate the reaction. Subsequently, **A** captures O_2 from air to produce

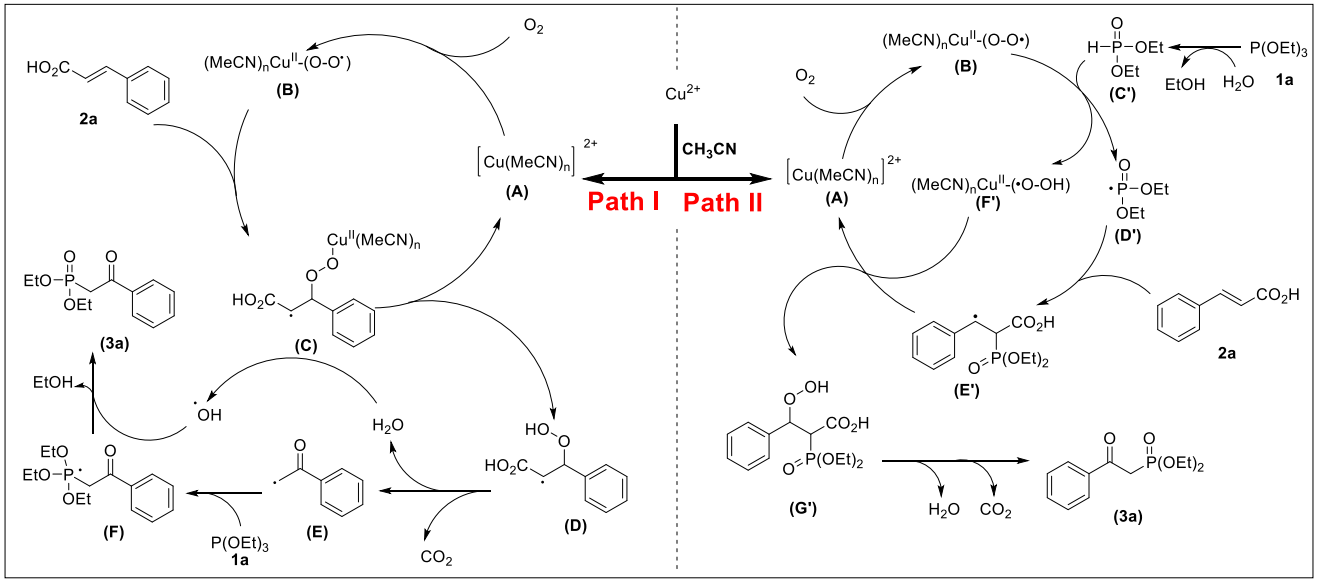
the copper-active-oxygen radical complex **B**, followed by attacking **2a** to afford the possible intermediate radical **C**. With the release of the complex **A**, radical **D** is generated *in-situ* from **C**. Afterwards, followed by the decarboxylation and dehydration reaction of **D**, the radical intermediate **E** is generated. Simultaneously, through the reaction of **E** with **1a**, the intermediate **F** is generated with the formation of a new P−C bond. Finally, the target product **3a** was obtained through the attack of hydroxyl radical with **F** *via* the Michaelis-Arbuzov rearrangement.

Scheme 7. Competitive reactions.



According to the above experimental results, due to the existence of a $(EtO)_2P(O)\bullet$ radical (**Scheme 6d**) and diethylphosphonate may work as a possible intermediate (**Scheme 6e**), another possible reaction pathway cannot be ruled out as shown in **Scheme 8 (path II)**. Firstly, triethylphosphite reacts with water from air to form diethylphosphonate (**C'**), which could react with the active-oxygen copper complex **B** derived from copper and oxygen to generate the intermediate radical $(EtO)_2P(O)\bullet$ (**D'**) and **F'**.[27] Simultaneously, **D** could attack the C-α position of cinnamic acid to form the intermediate **E'**. Furthermore,the hydroperoxide **G'** is formed through the reaction of **E'** with **F'**, where the copper(II) complex (**A**) is released and reused into the next catalytic cycle. Finally, through the breaking of the weak O-OH bond in the intermediate **G'** and decarboxylation reaction, the desired product **3a** was formed accordingly as the target product.

Scheme 8. Plausible mechanism.



Conclusions

In summary, we proposed a facile and convenient strategy for the synthesis of *β*-ketophosphine oxides, *β*-ketophosphinates and *β*-ketophosphonates using P(III)-nucleophiles as the phosphorylation reagents to react with aryl acrylic acids. A wide range of functionalized *β*-keto-organophosphorus compounds were obtained in good to excellent yields *via* the copper-catalyzed aerobic

oxidative/decarboxylative phosphorylation process. In addition, as verified by step-by-step control experiments, the reaction may be involved in a radical process and follow the second-order reaction kinetics. To the best of our knowledge, the copper-catalyzed aerobic oxidative/decarboxylative phosphorylation of aryl acrylic acids with P(III)-nucleophiles *via* the Michaelis-Arbuzov rearrangement has not been investigated previously. This method also exhibits a high potential value in synthesizing high value-added *β*-ketophosphine oxides, *β*-ketophosphinates and *β*-ketophosphonates, which may have wide applications in medicinal chemistry and functional material research.

Experimental Section

General Considerations:

All solvents used in the reactions were freshly distilled. Other commercially available reagents were used as received unless noted. The P(III)-nucleophiles were prepared according to the literature.[19b] ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (100 MHz), $^{31}P\{^{1}H\}$ (160 MHz) and $^{19}F\{^{1}H\}$ (376 MHz) were recorded on a 400 MHz Bruker spectrometer in $CDCl_3$. ^{1}H NMR chemical shifts were reported using TMS as the internal standard while ^{13}C NMR chemical shifts were reported relative to $CDCl_3$.

General procedure: A mixture of P(III)-nucleophiles (0.2 mmol), cinnamic acid derivatives (0.2 mmol) and $Cu(OTf)_2$ (10 mol%) were dissolved in a Schlenk tube containing CH_3CN (1.0 mL) and stirred at 100 °C for 12 h in an oil bath. Upon completion of the reaction, the mixture was concentrated under vacuum. Removal of the solvent under a reduced pressure gave the crude product; a pure product was obtained by passing the crude product through a short silica gel column using PE/EA (1:1-2:1) as eluent.

Single crystal preparation method: Single crystal of $C_{24}H_{25}O_2P$ (**3v**) was obtained by slow evaporation from the saturated solution of dichloromethane/*n*-hexane at room temperature.

***Diethyl (2-oxo-2-phenylethyl)phosphonate (3a)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3a** (45.1 mg, 0.176 mmol, 88%) as a yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.01-8.03 (m, 2H), 7.58-7.61 (m, 1H),

7.47-7.50 (m, 2H), 4.10-4.18 (m, 4H), 3.64 (d, *J* = 22.4 Hz, 2H), 1.28 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.0 (d, *J*(C,P) = 6.5 Hz), 136.6, 133.7, 129.1, 128.6, 62.7 (d, *J*(C,P) = 6.5 Hz), 38.5 (d, *J*(C,P) = 129.2 Hz), 16.3 (d, *J*(C,P) = 6.2 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.9.

***Dimethyl (2-oxo-2-phenylethyl)phosphonate (3b)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3b** (42.0 mg, 0.184 mmol, 92%) as a yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.00-8.01 (m, 2H), 7.59-7.62 (m, 1H), 7.47-7.51 (m, 2H), 3.78 (d, *J* = 11.2 Hz, 6H), 3.65 (d, *J* = 22.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 191.8 (d, *J*(C,P) = 6.6 Hz), 136.4 (d, *J*(C,P) = 2.6 Hz), 133.8, 129.0, 128.7, 53.2 (d, *J*(C,P) = 6.5 Hz), 37.5 (d, *J*(C,P) = 130.8 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 22.8.

***Dipropyl (2-oxo-2-phenylethyl)phosphonate (3c)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3c** (53.5 mg, 0.188 mmol, 94%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.01-8.03 (m, 2H), 7.58-7.61 (m, 1H), 7.46-7.50 (m, 2H), 4.00-4.06 (m, 4H), 3.65 (d, *J* = 22.8 Hz, 2H), 1.62-1.67 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.0 (d, *J*(C,P) = 6.7 Hz), 136.5 (d, *J*(C,P) = 1.9 Hz), 133.7, 129.1, 128.6, 68.1 (d, *J*(C,P) = 6.7 Hz), 38.3 (d, *J*(C,P) = 129.2 Hz), 23.7 (d, *J*(C,P) = 6.4 Hz), 9.9. $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.9. HRMS (ESI) m/z: calcd. For $C_{14}H_{23}O_4P$ $[M+H]^+$: 285.1251, found: 285.1246.

***Diisopropyl (2-oxo-2-phenylethyl)phosphonate (3d)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3d** (46.6 mg, 0.164 mmol, 82%) as a yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.01-8.03 (m, 2H), 7.56-7.60 (m, 1H), 7.45-7.49 (m, 2H), 4.68-4.77 (m, 2H), 3.59 (d, *J* = 23.2 Hz, 2H), 1.26-1.29 (m, 12H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.1 (d, *J*(C,P) = 6.7 Hz), 136.7, 133.5, 129.1, 128.5, 71.5 (d, *J*(C,P) = 6.7 Hz), 39.8 (d, *J*(C,P) = 129.6 Hz), 23.9 (dd, *J*(C,P) = 3.8 Hz, 19.6 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 17.7.

***Dibutyl (2-oxo-2-phenylethyl)phosphonate (3e)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3e** (56.9 mg, 0.182 mmol, 91%) as a yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.00-8.03 (m, 2H), 7.57-7.61 (m, 1H), 7.46-7.50 (m, 2H), 4.03-4.09 (m, 4H), 3.63 (d, *J* = 22.8 Hz, 2H), 1.56-1.63 (m, 4H), 1.30-1.36 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 191.9 (d, *J*(C,P) = 6.7 Hz), 136.6 (d, *J*(C,P) = 1.9 Hz), 133.6, 129.1, 128.6, 66.3 (d, *J*(C,P) = 6.7 Hz), 38.4 (d, *J*(C,P) = 128.7 Hz), 32.4 (d, *J*(C,P) = 6.3 Hz), 18.6, 13.5. ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 19.8.

***Diisobutyl (2-oxo-2-phenylethyl)phosphonate (3f)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3f** (55.6 mg, 0.178 mmol, 89%) as a yellow oil.[27c] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.01-8.03 (m, 2H), 7.57-7.61 (m, 1H), 7.46-7.50 (m, 2H), 3.81-3.87 (m, 4H), 3.65 (d, *J* = 22.8 Hz, 2H), 1.85-1.91 (m, 2H), 0.88 (d, *J* = 6.8 Hz, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 191.9 (d, *J*(C,P) = 6.7 Hz), 136.6 (d, *J*(C,P) = 1.7 Hz), 133.7, 129.1, 128.6, 72.4 (d, *J*(C,P) = 7.0 Hz), 38.2 (d, *J*(C,P) = 128.8 Hz), 29.2 (d, *J*(C,P) = 6.7 Hz), 18.6 (d, *J*(C,P) = 1.6 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 19.7.

***Dibenzyl (2-oxo-2-phenylethyl)phosphonate (3g)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3g** (60.1 mg, 0.158 mmol, 79%) as a yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.94-7.96 (m, 2H), 7.55-7.59 (m, 1H), 7.41-7.45 (m, 2H), 7.26-7.32 (m, 10H), 4.99-5.10 (m, 4H), 3.65 (d, *J* = 22.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 191.7 (d, *J*(C,P) = 6.6 Hz), 136.4 (d, *J*(C,P) = 2.5 Hz), 135.9 (d, *J*(C,P) = 6.4 Hz), 133.7, 129.0, 128.7, 128.6, 128.5, 128.1, 68.1 (d, *J*(C,P) = 6.3 Hz), 38.7 (d, *J*(C,P) = 130.7 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 21.1.

***Diphenyl (2-oxo-2-phenylethyl)phosphonate (3h)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3h** (60.6 mg, 0.172 mmol, 86%) as a yellow oil.[27c] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.04-8.06 (m, 2H), 7.60-7.64 (m, 1H), 7.48-7.52 (m, 2H), 7.29-7.33 (m, 4H), 7.15-7.19 (m, 6H), 3.94 (d, *J* = 22.8 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 190.7 (d, *J*(C,P) = 7.1 Hz), 150.0 (d, *J*(C,P) = 8.8 Hz), 136.4 (d, *J*(C,P)

= 2.5 Hz), 134.0, 129.8, 129.1, 128.8, 125.5, 120.6 (d, *J*(C,P) = 4.5 Hz), 37.8 (d, *J*(C,P) = 132.5 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 13.1.

***Dicyclopentyl (2-oxo-2-phenylethyl)phosphonate (3i)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3i** (50.5 mg, 0.150 mmol, 75%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.00-8.02 (m, 2H), 7.57-7.60 (m, 1H), 7.45-7.49 (m, 2H), 4.92-4.98 (m, 2H), 3.59 (d, *J* = 23.2 Hz, 2H), 1.74-1.78 (m, 8H), 1.53-1.67 (m, 8H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.1 (d, *J*(C,P) = 6.9 Hz), 136.7, 133.5, 129.1, 128.5, 80.1 (d, *J*(C,P) = 7.0 Hz), 39.5 (d, *J*(C,P) = 128.2 Hz), 34.1 (dd, *J*(C,P) = 3.9 Hz, 20.6 Hz), 23.0. $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 17.9. HRMS (ESI) m/z: calcd. For $C_{18}H_{26}O_4P$ $[M+H]^+$: 337.1564, found: 337.1558.

***Methyl (2-oxo-2-phenylethyl)(phenyl)phosphinate (3j)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3j** (51.0 mg, 0.186 mmol, 93%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.94-7.96 (m, 2H), 7.76-7.81 (m, 2H), 7.54-7.58 (m, 2H), 7.42-7.49 (m, 4H), 3.78-3.83 (m, 2H), 3.69 (d, *J* = 11.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.1 (d, *J*(C,P) = 5.6 Hz), 136.7 (d, *J*(C,P) = 1.1 Hz), 133.6, 132.9 (d, *J*(C,P) = 2.9 Hz), 132.0 (d, *J*(C,P) = 10.2 Hz), 129.3 (d, *J*(C,P) = 132.0 Hz), 129.1, 128.7 (d, *J*(C,P) = 13.2 Hz), 128.6, 51.8 (d, *J*(C,P) = 6.3 Hz), 42.6 (d, *J*(C,P) = 86.4 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 36.4. HRMS (ESI) m/z: calcd. For $C_{15}H_{16}O_3P$ $[M+H]^+$: 275.0832, found: 275.0824.

***Ethyl (2-oxo-2-phenylethyl)(phenyl)phosphinate (3k)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3k** (50.1 mg, 0.174 mmol, 87%) as a yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.95-7.97 (m, 2H), 7.76-7.81 (m, 2H), 7.53-7.58 (m, 2H), 7.42-7.48 (m, 4H), 3.92-4.16 (m, 2H), 3.77-3.83 (m, 2H), 1.26 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.2 (d, *J*(C,P) = 5.5 Hz), 136.8 (d, *J*(C,P) = 1.1 Hz), 133.6, 132.8 (d, *J*(C,P) = 2.9 Hz), 131.9 (d, *J*(C,P) = 10.3 Hz), 130.0 (d, *J*(C,P) = 132.2 Hz), 129.1,

128.7 (d, *J*(C,P) = 13.2 Hz), 128.6, 61.5 (d, *J*(C,P) = 6.2 Hz), 43.0 (d, *J*(C,P) = 86.1 Hz), 16.3 (d, *J*(C,P) = 6.6 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 34.6.

***Propyl (2-oxo-2-phenylethyl)(phenyl)phosphinate (3l)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3l** (51.4 mg, 0.170 mmol, 85%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.96-7.98 (m, 2H), 7.75-7.81 (m, 2H), 7.53-7.58 (m, 2H), 7.42-7.48 (m, 4H), 3.98-4.05 (m, 1H), 3.73-3.89 (m, 3H), 1.58-1.66 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.2 (d, *J*(C,P) = 5.5 Hz), 136.8 (d, *J*(C,P) = 0.9 Hz), 133.5, 132.7 (d, *J*(C,P) = 2.9 Hz), 132.1 (d, *J*(C,P) = 132.2 Hz), 131.9 (d, *J*(C,P) = 10.2 Hz), 129.1, 128.6 (d, *J*(C,P) = 13.2 Hz), 128.5, 66.9 (d, *J*(C,P) = 6.5 Hz), 43.0 (d, *J*(C,P) = 85.8 Hz), 23.8 (d, *J*(C,P) = 6.7 Hz), 10.0. ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 34.3. HRMS (ESI) m/z: calcd. For $C_{17}H_{20}O_3P$ $[M+H]^+$: 303.1145, found: 303.1140.

***Isobutyl (2-oxo-2-phenylethyl)(phenyl)phosphinate (3m)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3m** (51.9 mg, 0.164 mmol, 82%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.96-7.99 (m, 2H), 7.75-7.81 (m, 2H), 7.54-7.57 (m, 2H), 7.42-7.49 (m, 4H), 3.71-3.91 (m, 3H), 3.53-3.58 (m, 1H), 1.83-1.89 (m, 1H), 0.82-0.84 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.2 (d, *J*(C,P) = 5.7 Hz), 136.8, 133.5, 132.7 (d, *J*(C,P) = 2.8 Hz), 131.9 (d, *J*(C,P) = 10.1 Hz), 129.9 (d, *J*(C,P) = 132.0 Hz), 129.1, 128.6 (d, *J*(C,P) = 13.2 Hz), 128.5, 71.1 (d, *J*(C,P) = 6.6 Hz), 42.9 (d, *J*(C,P) = 85.8 Hz), 29.1 (d, *J*(C,P) = 6.9 Hz), 18.6 (d, *J*(C,P) = 7.4 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 34.1. HRMS (ESI) m/z: calcd. For $C_{18}H_{22}O_3P$ $[M+H]^+$: 317.1302, found: 317.1296.

***Benzyl (2-oxo-2-phenylethyl)(phenyl)phosphinate (3n)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3n** (53.9 mg, 0.154 mmol, 77%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.93-7.95 (m, 2H), 7.76-7.81 (m, 2H), 7.53-7.57 (m, 2H), 7.40-7.47 (m, 4H), 7.28-7.30 (m, 3H), 7.22-7.24 (m, 2H), 4.84-5.14 (m, 2H), 3.78-3.91 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.1 (d, *J*(C,P) = 5.5 Hz), 136.8, 135.9 (d, *J*(C,P) = 7.3 Hz), 133.6, 132.9 (d, *J*(C,P) = 2.9 Hz), 131.9 (d, *J*(C,P) = 10.3 Hz), 129.7

(d, *J*(C,P) = 131.7 Hz), 129.1, 128.7 (d, *J*(C,P) = 13.3 Hz), 128.6, 128.5,128.3, 127.8, 66.6 (d, *J*(C,P) = 5.9 Hz), 43.0 (d, *J*(C,P) = 85.7 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 35.6. HRMS (ESI) m/z: calcd. For $C_{21}H_{20}O_3P$ $[M+H]^+$: 351.1145, found: 351.1141.

***2-(Diphenylphosphoryl)-1-phenylethan-1-one (3o)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3o** (71.1 mg, 0.192 mmol, 96%) as a yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.97-7.99 (m, 2H), 7.78-7.83 (m, 4H), 7.40-7.56 (m, 9H), 4.15 (d, *J* = 15.6 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.9 (d, *J*(C,P) = 5.6 Hz), 137.0, 133.7, 132.2 (d, *J*(C,P) = 2.9 Hz), 131.9 (d, *J*(C,P) = 102.8 Hz), 131.1 (d, *J*(C,P) = 9.7 Hz), 129.3, 128.7, 128.6 (d, *J*(C,P) = 3.8 Hz), 43.3 (d, *J*(C,P) = 57.6 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 27.1.

***2-(Di-m-tolylphosphoryl)-1-phenylethan-1-one (3p)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3p** (64.2 mg, 0.184 mmol, 92%) as a colorless oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.97-7.99 (m, 2H), 7.51-7.65 (m, 5H), 7.32-7.43 (m, 6H), 4.12 (d, *J* = 15.2 Hz, 2H), 2.35 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 192.9 (d, *J*(C,P) = 5.6 Hz), 138.6 (d, *J*(C,P) = 12.0 Hz), 137.1, 133.5, 132.9 (d, *J*(C,P) = 3.0 Hz), 131.9 (d, *J*(C,P) = 102.2 Hz), 131.6 (d, *J*(C,P) = 9.4 Hz), 129.3, 128.5, 128.4 (d, *J*(C,P) = 13.0 Hz), 128.1 (d, *J*(C,P) = 10.0 Hz), 43.4 (d, *J*(C,P) = 57.0 Hz), 21.4. $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 27.3.

***2-(Di-p-tolylphosphoryl)-1-phenylethan-1-one (3q)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3q** (66.2 mg, 0.190 mmol, 95%) as a colorless oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.98-8.01 (m, 2H), 7.65-7.70 (m, 4H), 7.51-7.55 (m, 1H), 7.39-7.43 (m, 2H), 7.24-7.27 (m, 4H), 4.10 (d, *J* = 15.2 Hz, 2H), 2.38 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 193.1 (d, *J*(C,P) = 5.6 Hz), 142.6 (d, *J*(C,P) = 2.9 Hz), 137.1, 133.5, 131.1 (d, *J*(C,P) = 10.1 Hz), 129.4, 129.3 (d, *J*(C,P) = 3.4 Hz), 128.9 (d, *J*(C,P) = 105.0 Hz), 128.5, 43.7 (d, *J*(C,P) = 57.3 Hz), 21.6 (d, *J*(C,P) = 1.1 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 27.2.

***2-(Bis(4-ethylphenyl)phosphoryl)-1-phenylethan-1-one (3r)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3r** (73.0 mg, 0.194 mmol, 97%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.97-7.99 (m, 2H), 7.68-7.73 (m, 4H), 7.50-7.54 (m, 1H), 7.38-7.42 (m, 2H), 7.26-7.29 (m, 4H), 4.11 (d, *J* = 15.2 Hz, 2H), 2.64-2.70 (m, 4H), 1.23 (t, *J* = 7.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.1 (d, *J*(C,P) = 5.6 Hz), 148.8 (d, *J*(C,P) = 2.8 Hz), 137.1, 133.5, 131.2 (d, *J*(C,P) = 10.1 Hz), 129.3, 129.1 (d, *J*(C,P) = 105.1 Hz), 128.5, 128.2 (d, *J*(C,P) = 12.6 Hz), 43.6 (d, *J*(C,P) = 57.2 Hz), 28.9, 15.1. ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 27.2. HRMS (ESI) m/z: calcd. For $C_{24}H_{26}O_2P$ $[M+H]^+$: 377.1665, found: 377.1659.

***2-(Bis(4-butylphenyl)phosphoryl)-1-phenylethan-1-one (3s)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3s** (80.5 mg, 0.186 mmol, 93%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.96-7.98 (m, 2H), 7.66-7.71 (m, 4H), 7.50-7.54 (m, 1H), 7.38-7.42 (m, 2H), 7.24-7.26 (m, 4H), 4.11 (d, *J* = 15.6 Hz, 2H), 2.62 (t, *J* = 7.8 Hz, 4H), 1.54-1.62 (m, 4H), 1.30-1.36 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.1 (d, *J*(C,P) = 5.6 Hz), 147.5 (d, *J*(C,P) = 2.8 Hz), 137.1, 133.5, 131.2 (d, *J*(C,P) = 10.1 Hz), 129.3, 129.0 (d, *J*(C,P) = 110.4 Hz), 128.7 (d, *J*(C,P) = 5.7 Hz), 128.5, 43.7 (d, *J*(C,P) = 57.2 Hz), 35.6, 33.2, 22.3, 13.9. ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 27.3. HRMS (ESI) m/z: calcd. For $C_{28}H_{34}O_2P$ $[M+H]^+$: 433.2291, found: 433.2284.

***2-(Bis(4-(tert-butyl)phenyl)phosphoryl)-1-phenylethan-1-one (3t)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3t** (78.7 mg, 0.182 mmol, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.95-7.97 (m, 2H), 7.70-7.75 (m, 4H), 7.44-7.53 (m, 5H), 7.37-7.41 (m, 2H), 4.11 (d, *J* = 15.2 Hz, 2H), 1.30 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.2 (d, *J*(C,P) = 5.5 Hz), 155.5 (d, *J*(C,P) = 2.8 Hz), 137.1, 133.4, 131.0 (d, *J*(C,P) = 10.1 Hz), 129.3, 128.8 (d, *J*(C,P) = 105.2 Hz), 128.4, 125.6 (d, *J*(C,P) = 12.4 Hz), 43.7 (d, *J*(C,P) = 57 Hz), 35.0, 31.1. ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 26.7. HRMS (ESI) m/z: calcd. For $C_{28}H_{34}O_2P$ $[M+H]^+$: 433.2291, found: 433.2282.

***2-(Bis(4-methoxyphenyl)phosphoryl)-1-phenylethan-1-one (3u)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3u** (68.4 mg, 0.180 mmol, 90%) as a colorless oil.[18] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.98-7.99 (m, 2H), 7.68-7.73 (m, 4H), 7.52-7.55 (m, 1H), 7.40-7.43 (m, 2H), 6.94-6.96 (m, 4H), 4.09 (d, *J* = 15.6 Hz, 2H), 3.82 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.3 (d, *J*(C,P) = 5.5 Hz), 162.5 (d, *J*(C,P) = 2.9 Hz), 137.1, 133.5, 133.0 (d, *J*(C,P) = 11.2 Hz), 129.3, 128.5, 123.3 (d, *J*(C,P) = 109.6 Hz), 114.2 (d, *J*(C,P) = 13.2 Hz), 55.4, 43.9 (d, *J*(C,P) = 57.6 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 27.2.

***2-(Bis(3,5-dimethylphenyl)phosphoryl)-1-phenylethan-1-one (3v)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3v** (64.0 mg, 0.170 mmol, 85%) as a white solid,[8b] mp: 109–111°C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.97-7.99 (m, 2H), 7.51-7.54 (m, 1H), 7.37-7.43 (m, 6H), 7.12 (s, 2H), 4.10 (d, *J* = 15.2 Hz, 2H), 2.32 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.3 (d, *J*(C,P) = 5.6 Hz), 138.3 (d, *J*(C,P) = 12.9 Hz), 137.2, 133.9 (d, *J*(C,P) = 2.9 Hz), 133.5, 129.3, 123.3 (d, *J*(C,P) = 101.8 Hz), 128.6 (d, *J*(C,P) = 9.7 Hz), 128.5, 43.4 (d, *J*(C,P) = 56.4 Hz), 21.3. ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 27.6.

***2-(Di([1,1'-biphenyl]-3-yl)phosphoryl)-1-phenylethan-1-one (3w)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3w** (77.5 mg, 0.164 mmol, 82%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.07-8.10 (m, 2H), 7.99-8.01 (m, 2H), 7.73-7.81 (m, 4H), 7.50-7.57 (m, 7H), 7.34-7.45 (m, 8H), 4.24 (d, *J* = 15.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.9 (d, *J*(C,P) = 5.4 Hz), 141.8 (d, *J*(C,P) = 12.1 Hz), 139.9, 137.0, 133.7, 132.5 (d, *J*(C,P) = 102.1 Hz), 131.0 (d, *J*(C,P) = 2.9 Hz), 129.89 (d, *J*(C,P) = 1.3 Hz), 129.88 (d, *J*(C,P) = 18.4 Hz), 129.3, 129.1 (d, *J*(C,P) = 12.9 Hz), 128.9, 128.6, 127.9, 127.3, 43.5 (d, *J*(C,P) = 57.2 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 27.2. HRMS (ESI) m/z: calcd. For $C_{32}H_{26}O_2P$ $[M+H]^+$: 473.1665, found: 473.1661.

***2-(Bis(4-chlorophenyl)phosphoryl)-1-phenylethan-1-one (3x)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3x** (69.3 mg, 0.178 mmol, 89%) as a colorless oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.95-7.97 (m, 2H), 7.70-7.75 (m, 4H), 7.55-7.59 (m, 1H), 7.42-7.46 (m, 6H), 4.13 (d, *J* = 15.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.5 (d, *J*(C,P) = 5.5 Hz), 139.1 (d, *J*(C,P) = 3.4 Hz), 136.7, 133.9, 132.5 (d, *J*(C,P) = 10.7 Hz), 130.1 (d, *J*(C,P) = 104.5 Hz), 129.2, 129.1, 128.7, 43.1 (d, *J*(C,P) = 59.6 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 26.1.

***2-(Bis(4-fluorophenyl)phosphoryl)-1-phenylethan-1-one (3y)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3y** (62.0 mg, 0.174 mmol, 87%) as a colorless oil.[18] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.95-7.97 (m, 2H), 7.77-7.84 (m, 4H), 7.54-7.58 (m, 1H), 7.41-7.45 (m, 2H), 7.13-7.18 (m, 4H), 4.14 (d, *J* = 16.0 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.7 (d, *J*(C,P) = 5.5 Hz), 165.2 (dd, ^{1}*J*(C,F) = 252.9 Hz), ^{2}*J*(C,P) = 3.4 Hz), 136.7, 133.9, 133.8 (dd, ^{1}*J*(C,F) =11.3 Hz), ^{2}*J*(C,P) = 8.9 Hz), 129.2, 128.7, 127.7 (dd, ^{1}*J*(C,F) =3.5 Hz), ^{2}*J*(C,P) = 106.4 Hz), 116.2 (dd, ^{1}*J*(C,F) =21.4 Hz), ^{2}*J*(C,P) = 13.5 Hz), 43.3 (d, *J*(C,P) = 59.3 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 26.1.

***2-(Bis(3-fluorophenyl)phosphoryl)-1-phenylethan-1-one (3z)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3z** (59.8 mg, 0.168 mmol, 84%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.96-7.98 (m, 2H), 7.42-7.62 (m, 9H), 7.21-7.27 (m, 2H), 4.14 (d, *J* = 15.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.2 (d, *J*(C,P) = 5.7 Hz), 162.7 (dd, ^{1}*J*(C,F) = 249.5 Hz), ^{2}*J*(C,P) = 17.3 Hz), 136.7, 134.2 (dd, ^{1}*J*(C,F) = 5.6 Hz), ^{2}*J*(C,P) = 102.3 Hz), 133.9, 130.8 (dd, ^{1}*J*(C,F) = 14.4 Hz), ^{2}*J*(C,P) = 7.4 Hz), 129.2, 128.7, 126.8 (dd, ^{1}*J*(C,F) = 9.3 Hz), ^{2}*J*(C,P) = 3.3 Hz), 119.7 (dd, ^{1}*J*(C,F) = 21.0 Hz), ^{2}*J*(C,P) = 2.6 Hz), 118.2 (dd, ^{1}*J*(C,F) = 22.6 Hz), ^{2}*J*(C,P) = 10.6 Hz), 42.8 (d, *J*(C,P) = 60.1 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 25.0 (d, *J*(P,F) = 5.8 Hz). ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = −110.3 (d, *J*(P,F) = 6.0 Hz). HRMS (ESI) m/z: calcd. For $C_{20}H_{16}F_2O_2P$ $[M+H]^+$: 357.0851, found: 357.0844.

***2-(Di(naphthalen-1-yl)phosphoryl)-1-phenylethan-1-one (3aa)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3aa** (76.5 mg, 0.182 mmol, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.73-8.71 (m, 2H), 7.97-8.05 (m, 4H), 7.79-7.86 (m, 4H), 7.39-7.50 (m, 7H), 7.22-7.26 (m, 2H), 4.48 (d, *J* = 15.6 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.3 (d, *J*(C,P) = 5.3 Hz), 137.0, 133.9 (d, *J*(C,P) = 9.4 Hz), 133.5 (d, *J*(C,P) = 3.0 Hz), 133.4 (d, *J*(C,P) = 8.8 Hz), 133.3, 132.6 (d, *J*(C,P) = 11.0 Hz), 129.1 (d, *J*(C,P) = 1.2 Hz), 129.0, 128.8 (d, *J*(C,P) = 100.2 Hz), 128.2, 127.5, 126.6 (d, *J*(C,P) = 5.3 Hz), 126.5, 124.5 (d, *J*(C,P) = 14.4 Hz), 43.4 (d, *J*(C,P) = 57.9 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 32.5. HRMS (ESI) m/z: calcd. For $C_{28}H_{22}O_2P$ $[M+H]^+$: 421.1352, found: 421.1343.

***2-(Di(naphthalen-2-yl)phosphoryl)-1-phenylethan-1-one (3ab)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3ab** (74.0 mg, 0.176 mmol, 88%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.46-8.49 (m, 2H), 8.00-8.02 (m, 2H), 7.77-7.91 (m, 8H), 7.47-7.59 (m, 5H), 7.35-7.39 (m, 2H), 4.32 (d, *J* = 15.2 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.9 (d, *J*(C,P) = 5.7 Hz), 137.0, 134.8, 133.7, 133.3 (d, *J*(C,P) = 8.9 Hz), 132.5 (d, *J*(C,P) = 13.3 Hz), 129.6, 129.2 (d, *J*(C,P) = 27.6 Hz), 128.7, 128.6, 128.4, 127.9, 127.1, 125.8 (d, *J*(C,P) = 11.0 Hz), 43.3 (d, *J*(C,P) = 57.7 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 27.3. HRMS (ESI) m/z: calcd. For $C_{28}H_{21}O_2P$ $[M+H]^+$: 421.1352, found: 421.1346.

***(R)-2-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)-1-phenylethan-1-one (3ac)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3ac** (46.3 mg, 0.166 mmol, 83%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.87-8.00 (m, 5H), 7.68-7.72 (m, 1H), 7.49-7.57 (m, 2H), 7.40-7.43 (m, 2H), 7.31-7.35 (m, 1H), 7.22-7.26 (m, 1H), 7.11-7.13 (m, 1H), 3.88 (d, *J* = 18.4 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 191.4 (d, *J*(C,P) = 5.4 Hz), 149.1 (d, *J*(C,P) = 8.3 Hz), 136.5 (d, *J*(C,P) = 1.8 Hz), 135.9 (d, *J*(C,P) = 6.8 Hz), 133.8, 131.0 (d, *J*(C,P) = 10.4 Hz), 130.7, 128.9, 128.7, 128.6, 128.5, 125.2, 124.9, 123.8 (d, *J*(C,P) = 10.3 Hz), 123.7 (d, *J*(C,P) = 126.2 Hz), 122.1 (d, *J*(C,P) = 11.3 Hz), 120.5 (d, *J*(C,P) = 6.5 Hz), 41.6 (d,

J(C,P) = 84.2 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 28.6. HRMS (ESI) m/z: calcd. For $C_{20}H_{16}O_3P$ $[M+H]^+$: 335.0832, found: 335.0823.

***2-(Dicyclohexylphosphoryl)-1-phenylethan-1-one (3ad)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **3ad** (49.9 mg, 0.150 mmol, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.05-8.07 (m, 2H), 7.58-7.61 (m, 1H), 7.47-7.51 (m, 2H), 3.55 (d, *J* = 14.4 Hz, 2H), 1.84-2.02 (m, 11H), 1.22-1.29 (m, 11H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 194.9 (d, *J*(C,P) = 4.7 Hz), 137.2 (d, *J*(C,P) = 1.7 Hz), 133.7, 129.1, 128.7, 37.0 (d, *J*(C,P) = 46.2 Hz), 36.7 (d, *J*(C,P) = 64.5 Hz), 26.5 (dd, *J*(C,P) = 5.4 Hz, 12.9 Hz), 25.9 (d, *J*(C,P) = 1.3 Hz), 25.6 (dd, *J*(C,P) = 3.1 Hz, 36.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 50.7. HRMS (ESI) m/z: calcd. For $C_{20}H_{30}O_2P$ $[M+H]^+$: 333.1978, found: 333.1973.

***Diethyl (2-oxo-2-(p-tolyl)ethyl)phosphonate (4a)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4a** (47.6 mg, 0.176 mmol, 88%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.90-7.92 (m, 2H), 7.26-7.28 (m, 2H), 4.10-4.17 (m, 4H), 3.61 (d, *J* = 22.8 Hz, 2H), 2.42 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 191.5 (d, *J*(C,P) = 6.5 Hz), 144.7, 134.1 (d, *J*(C,P) = 1.9 Hz), 129.3, 129.2, 62.6 (d, *J*(C,P) = 6.4 Hz), 38.4 (d, *J*(C,P) = 129.3 Hz), 21.7, 16.3 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.2.

***Diethyl (2-(4-methoxyphenyl)-2-oxoethyl)phosphonate (4b)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4b** (49.2 mg, 0.172 mmol, 86%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.99-8.01 (m, 2H), 6.93-6.96 (m, 2H), 4.10-4.17 (m, 4H), 3.88 (s, 3H), 3.59 (d, *J* = 22.8 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.3 (d, *J*(C,P) = 6.2 Hz), 164.0, 131.5, 129.6, 113.8, 62.7 (d, *J*(C,P) = 6.4 Hz), 55.5, 38.2 (d, *J*(C,P) = 129.2 Hz), 16.2 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 20.5.

***Diethyl (2-oxo-2-(o-tolyl)ethyl)phosphonate (4c)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4c** (43.8 mg, 0.162 mmol, 81%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.74-7.76 (m, 1H), 7.38-7.41 (m, 1H), 7.24-7.30 (m, 2H), 4.08-4.15 (m, 4H), 3.59 (d, *J* = 22.4 Hz, 2H), 2.52 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 195.1 (d, *J*(C,P) = 6.5 Hz), 139.0, 137.3 (d, *J*(C,P) = 1.9 Hz), 132.0, 131.9, 129.6, 125.7, 62.5 (d, *J*(C,P) = 6.3 Hz), 41.1 (d, *J*(C,P) = 128.6 Hz), 21.3, 16.2 (d, *J*(C,P) = 6.3 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 20.2. HRMS (ESI) m/z: calcd. For $C_{13}H_{20}O_4P$ $[M+H]^+$: 271.1094, found: 271.1090.

***Diethyl (2-(2-methoxyphenyl)-2-oxoethyl)phosphonate (4d)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4d** (48.6 mg, 0.170 mmol, 85%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.70-7.73 (m, 1H), 7.46-7.51 (m, 1H), 6.96-7.03 (m, 2H), 4.06-4.133 (m, 4H), 3.93 (s, 3H), 3.82 (d, *J* = 22.0 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.4 (d, *J*(C,P) = 7.2 Hz), 158.7, 134.2, 130.9, 127.7 (d, *J*(C,P) = 2.3 Hz), 120.8, 111.5, 62.2 (d, *J*(C,P) = 6.3 Hz), 55.6, 42.5 (d, *J*(C,P) = 129.5 Hz), 16.2 (d, *J*(C,P) = 6.4 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 21.2. HRMS (ESI) m/z: calcd. For $C_{13}H_{20}O_5P$ $[M+H]^+$: 287.1043, found: 287.1036.

***Diethyl (2-oxo-2-(m-tolyl)ethyl)phosphonate (4e)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4e** (43.2 mg, 0.160 mmol, 80%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.80-7.82 (m, 2H), 7.35-7.41 (m, 2H), 4.10-4.18 (m, 4H), 3.62 (d, *J* = 22.8 Hz, 2H), 2.42 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 192.1 (d, *J*(C,P) = 6.5 Hz), 138.4, 136.6 (d, *J*(C,P) = 2.0 Hz), 134.4, 129.5, 128.5, 126.4, 62.6 (d, *J*(C,P) = 6.5 Hz), 38.5 (d, *J*(C,P) = 129.3 Hz), 21.3, 16.2 (d, *J*(C,P) = 6.4 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 20.0.

***Diethyl (2-(3-methoxyphenyl)-2-oxoethyl)phosphonate (4f)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4f** (48.7 mg, 0.170 mmol, 85%) as a pale yellow oil.[28] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.59-7.61 (m, 1H),

7.53-7.54 (m, 1H), 7.37-7.41 (m, 1H), 7.13-7.15 (m, 1H), 4.11-4.18 (m, 4H), 3.86 (s, 3H), 3.62 (d, *J* = 22.8 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 191.8 (d, *J*(C,P) = 6.6 Hz), 159.8, 137.9 (d, *J*(C,P) = 2.0 Hz), 129.6, 121.9, 120.4, 112.8, 62.7 (d, *J*(C,P) = 6.5 Hz), 55.5, 38.6 (d, *J*(C,P) = 129.5 Hz), 16.3 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.9.

***Diethyl (2-(4-fluorophenyl)-2-oxoethyl)phosphonate (4g)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4g** (44.4 mg, 0.162 mmol, 81%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.04-8.08 (m, 2H), 7.13-7.17 (m, 2H), 4.10-4.18 (m, 4H), 3.60 (d, *J* = 22.8 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.3 (d, *J*(C,P) = 6.4 Hz), 166.1 (d, ^{1}J(C,F) = 254.5 Hz), 133.0 (dd, ^{1}J(C,F) = 2.8 Hz), ^{2}J(C,P) = 1.7 Hz), 131.9 (d, ^{1}J(C,F) = 9.4 Hz), 115.8 (d, ^{1}J(C,F) = 21.9 Hz), 62.7 (d, *J*(C,P) = 6.5 Hz), 38.6 (d, *J*(C,P) = 128.7 Hz), 16.2 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.6. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = −104.1 (s).

***Diethyl (2-(4-chlorophenyl)-2-oxoethyl)phosphonate (4h)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4h** (41.9 mg, 0.144 mmol, 72%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.96-7.98 (m, 2H), 7.45-7.47 (m, 2H), 4.10-4.18 (m, 4H), 3.60 (d, *J* = 22.8 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.8 (d, *J*(C,P) = 6.5 Hz), 140.3, 134.8 (d, *J*(C,P) = 1.7 Hz), 130.5, 128.9, 62.8 (d, *J*(C,P) = 6.5 Hz), 38.6 (d, *J*(C,P) = 128.6 Hz), 16.2 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.4.

***Diethyl (2-(4-bromophenyl)-2-oxoethyl)phosphonate (4i)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4i** (49.6 mg, 0.148 mmol, 74%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.88-7.90 (m, 2H), 7.64-7.61 (m, 2H), 4.10-4.17 (m, 4H), 3.60 (d, *J* = 22.8 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 191.0 (d, *J*(C,P) = 6.6 Hz), 135.2 (d, *J*(C,P) = 1.7 Hz), 131.9,

130.6, 129.1, 62.8 (d, *J*(C,P) = 6.5 Hz), 38.6 (d, *J*(C,P) = 128.6 Hz), 16.3 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.4.

***Diethyl (2-(4-nitrophenyl)-2-oxoethyl)phosphonate (4j)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4j** (41.0 mg, 0.136 mmol, 68%) as a pale yellow oil.[25c] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.32-8.34 (m, 2H), 8.19-8.21 (m, 2H), 4.12-4.19 (m, 4H), 3.67 (d, *J* = 23.2 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.6 (d, *J*(C,P) = 6.7 Hz), 150.6, 140.8, 130.2, 123.8, 63.0 (d, *J*(C,P) = 6.5 Hz), 38.6 (d, *J*(C,P) = 127.9 Hz), 16.3 (d, *J*(C,P) = 6.2 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.4.

***Diethyl (2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)phosphonate (4k)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4k** (44.7 mg, 0.138 mmol, 69%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.13-8.15 (m, 2H), 7.74-7.76 (m, 2H), 4.11-4.19 (m, 4H), 3.66 (d, *J* = 22.8 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 191.1 (d, *J*(C,P) = 6.7 Hz), 139.1, 134.9 (d, ^{1}J(C,F) = 32.6 Hz), 129.4, 125.7 (dd, ^{1}J(C,F) = 7.3 Hz), ^{2}J(C,P) = 3.6 Hz), 123.5 (d, ^{1}J(C,F) = 271.1 Hz), 62.8 (d, *J*(C,P) = 6.5 Hz), 38.9 (d, *J*(C,P) = 128.5 Hz), 16.2 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.0. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = −63.2.

***Diethyl (2-(2-fluorophenyl)-2-oxoethyl)phosphonate (4l)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4l** (42.2 mg, 0.154 mmol, 77%) as a pale yellow oil.[9] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.85-7.89 (m, 1H), 7.52-7.58 (m, 1H), 7.22-7.28 (m, 1H), 7.12-7.17 (m, 1H), 4.10-4.17 (m, 4H), 3.71 (d, *J* = 22.0 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): 190.1 (dd, ^{1}J(C,F) = 7.3 Hz), ^{2}J(C,P) = 3.1 Hz), 161.8 (d, ^{1}J(C,F) = 253.3 Hz), 135.2 (d, ^{1}J(C,F) = 9.2 Hz), 131.1 (d, ^{1}J(C,F) = 1.7 Hz), 125.5 (dd, ^{1}J(C,F) = 11.3 Hz), ^{2}J(C,P) = 2.0 Hz), 124.6 (d, ^{1}J(C,F) = 3.4 Hz), 116.7 (d, ^{1}J(C,F) = 23.7 Hz), 62.5 (d, *J*(C,P) = 6.3 Hz), 42.5 (dd, ^{1}J(C,F) = 7.8 Hz), ^{2}J(C,P) = 129.5 Hz), 16.2 (d, *J*(C,P) =

6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.8. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = −109.9.

***Diethyl (2-(2-bromophenyl)-2-oxoethyl)phosphonate (4m)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4m** (50.9 mg, 0.152 mmol, 76%) as a pale yellow oil.[10b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.60-7.63 (m, 1H), 7.54-7.57 (m, 1H), 7.37-7.41 (m, 1H), 7.30-7.34 (m, 1H), 4.08-4.16 (m, 4H), 3.70 (d, *J* = 22.4 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 195.1 (d, *J*(C,P) = 6.8 Hz), 140.8 (d, *J*(C,P) = 1.6 Hz), 133.7, 132.2, 129.8, 127.5, 119.0, 62.7 (d, *J*(C,P) = 6.3 Hz), 42.0 (d, *J*(C,P) = 127.2 Hz), 16.2 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.9.

***Diethyl (2-(3-fluorophenyl)-2-oxoethyl)phosphonate (4n)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4n** (40.5 mg, 0.148 mmol, 74%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.80-7.82 (m, 1H), 7.69-7.72 (m, 1H), 7.45-7.50 (m, 1H), 7.28-7.32 (m, 1H), 4.11-4.18 (m, 4H), 3.61 (d, *J* = 22.8 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.8 (dd, ^{1}J(C,F) = 6.6 Hz), ^{2}J(C,P) = 2.3 Hz), 162.8 (d, ^{1}J(C,F) = 246.7 Hz), 138.6 (dd, ^{1}J(C,F) = 6.3 Hz), ^{2}J(C,P) = 1.8 Hz), 130.3 (d, ^{1}J(C,F) = 7.6 Hz), 125.0 (d, ^{1}J(C,F) = 3.0 Hz), 120.7 (d, ^{1}J(C,F) = 21.3 Hz), 115.6 (d, ^{1}J(C,F) = 22.5 Hz), 62.8 (d, *J*(C,P) = 6.5 Hz), 38.8 (d, *J*(C,P) =128.9 Hz), 16.2 (d, *J*(C,P) = 6.3 Hz). ^{31}P NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.2. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = −111.7.

***Diethyl (2-(3-bromophenyl)-2-oxoethyl)phosphonate (4o)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4o** (50.9 mg, 0.152 mmol, 76%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 8.14-8.15 (m, 1H), 7.94-7.96 (m, 1H), 7.70-7.73 (m, 1H), 7.35-7.39 (m, 1H), 4.11-4.19 (m, 4H), 3.60 (d, *J* = 23.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 190.7 (d, *J*(C,P) = 6.6 Hz), 138.2 (d, *J*(C,P) = 1.7 Hz), 136.5, 132.0, 130.2, 127.7, 122.9, 62.8 (d, *J*(C,P) = 6.5 Hz), 38.7 (d, *J*(C,P) = 128.7 Hz), 16.2 (d, *J*(C,P) = 6.3 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.1. HRMS (ESI) m/z: calcd. For $C_{12}H_{17}BrO_4P$ $[M+H]^+$: 335.0043, found: 335.0035.

***Diethyl (2-oxo-2-(3-(trifluoromethyl)phenyl)ethyl)phosphonate (4p)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4p** (46.1 mg, 0.142 mmol, 71%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.21-8.28 (m, 2H), 7.84-7.86 (m, 1H), 7.62-7.66 (m, 1H), 4.11-4.20 (m, 4H), 3.66 (d, *J* = 23.2 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 190.7 (d, *J*(C,P) = 6.7 Hz), 138.2 (d, *J*(C,P) = 1.6 Hz), 132.3, 131.3 (d, ^{1}*J*(C,F) = 32.8 Hz), 130.2 (d, ^{1}*J*(C,F) = 3.5 Hz), 129.3, 125.9 (d, ^{1}*J*(C,F) = 3.8 Hz), 123.6 (d, ^{1}*J*(C,F) = 270.9 Hz), 62.8 (d, *J*(C,P) = 6.5 Hz), 38.8 (d, *J*(C,P) = 128.3 Hz), 16.2 (d, *J*(C,P) = 6.4 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 18.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = −62.9. HRMS (ESI) m/z: calcd. For $C_{13}H_{17}F_3O_4P$ $[M+H]^+$: 325.0812, found: 325.0806.

***Diethyl (2-(2-bromo-4-fluorophenyl)-2-oxoethyl)phosphonate (4q)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4q** (55.1 mg, 0.156 mmol, 78%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.63-7.67 (m, 1H), 7.36-7.39 (m, 1H), 7.09-7.14 (m, 1H), 4.09-4.17 (m, 4H), 3.68 (d, *J* = 22.4 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.6 (d, *J*(C,P) = 6.7 Hz), 163.5 (d, ^{1}*J*(C,F) = 255.3 Hz), 136.7, 131.9 (d, ^{1}*J*(C,F) = 9.2 Hz), 121.3 (d, ^{1}*J*(C,F) = 24.5 Hz), 120.4 (d, ^{1}*J*(C,F) = 9.9 Hz), 114.8 (d, ^{1}*J*(C,F) = 21.2 Hz), 62.7 (d, *J*(C,P) = 6.4 Hz), 41.9 (d, *J*(C,P) = 127.2 Hz), 16.2 (d, *J*(C,P) = 6.2 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 18.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C, TMS): δ = −106.1. HRMS (ESI) m/z: calcd. For $C_{12}H_{16}BrFO_4P$ $[M+H]^+$: 352.9949, found: 352.9944.

***Diethyl (2-(2,5-dichlorophenyl)-2-oxoethyl)phosphonate (4r)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4r** (48.8 mg, 0.150 mmol, 75%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.55-7.56 (m, 1H), 7.34-7.40 (m, 2H), 4.10-4.17 (m, 4H), 3.69 (d, *J* = 22.4 Hz, 2H), 1.29 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.2 (d, *J*(C,P) = 7.0 Hz), 139.8 (d, *J*(C,P) = 1.5 Hz), 133.1, 132.1, 131.6, 129.8, 129.2, 62.8 (d, *J*(C,P) = 6.4 Hz), 42.1 (d, *J*(C,P) = 127.5 Hz), 16.2 (d, *J*(C,P) = 6.3

Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 18.6. HRMS (ESI) m/z: calcd. For $C_{12}H_{16}Cl_2O_4P$ $[M+H]^+$: 325.0158, found: 325.0153.

***Diethyl (S)-(1-oxo-1-phenylpropan-2-yl)phosphonate (4s)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4s** (44.4 mg, 0.164 mmol, 82%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.45-7.49 (m, 2H), 7.30-7.38 (m, 3H), 4.42 (d, *J* = 23.6 Hz, 1H), 3.93-4.12 (m, 4H), 2.31 (s, 3H), 1.17-1.28 (m, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 201.2 (d, *J*(C,P) = 4.4 Hz), 131.0 (d, *J*(C,P) = 7.8 Hz), 129.8 (d, *J*(C,P) = 7.0 Hz), 128.8 (d, *J*(C,P) = 2.0 Hz), 128.0 (d, *J*(C,P) = 2.7 Hz), 63.1 (dd, *J*(C,P) = 6.8 Hz, 46.7 Hz), 60.1 (d, *J*(C,P) = 131.7 Hz), 30.7 (d, *J*(C,P) = 2.8 Hz), 16.3 (dd, *J*(C,P) = 4.9 Hz, 5.9 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 19.0.

2-(Diphenylphosphoryl)-1-(furan-2-yl)ethan-1-one (4t): According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **4t** (37.2 mg, 0.104 mmol, 52%) as a colorless oil.[8b] ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.78−7.83 (m, 4H), 7.44−7.54 (m, 7H), 7.29−7.30 (m, 1H), 6.47-6.48 (m, 1H), 4.01-4.05 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 180.6 (d, *J*(C,P) = 1.9 Hz), 152.6, 147.3, 132.3 (d, *J*(C,P) = 2.7 Hz), 131.6 (d, *J*(C,P) = 110.4 Hz), 131.2 (d, *J*(C,P) = 9.8 Hz), 128.7 (d, *J*(C,P) = 12.3 Hz), 119.7, 112.8, 43.1 (d, *J*(C,P) = 57.4 Hz); $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 27.6.

***Diethyl (2,2-diphenylvinyl)phosphonate (10a)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **10a** (29.1 mg, 0.092 mmol, 46%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 7.27-7.38 (m, 10H), 6.19 (d, *J* = 15.6 Hz, 1H), 3.77-3.97 (m, 4H), 1.13 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 25 °C, TMS): δ = 160.1 (d, *J*(C,P) = 6.0 Hz), 141.6 (d, *J*(C,P) = 22.1 Hz), 139.0 (d, *J*(C,P) = 7.4 Hz), 129.8 (d, *J*(C,P) = 1.5 Hz), 129.4, 128.6, 128.3, 128.2, 127.8, 114.9 (d, *J*(C,P) = 192.1 Hz), 61.5 (d, *J*(C,P) = 6.0 Hz), 16.2 (d, *J*(C,P) = 6.7 Hz). $^{31}P\{^{1}H\}$ NMR (160 MHz, $CDCl_3$, 25 °C, TMS): δ = 16.6. HRMS (ESI) m/z: calcd. For $C_{18}H_{22}O_3P$ $[M+H]^+$: 317.1302, found: 317.1294.

***Diethyl (Z)-(2-phenyl-2-(2-(phenylsulfonyl)hydrazineylidene)ethyl)phosphonate (12a)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **12a** (70.6 mg, 0.172 mmol, 86%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 10.23 (s, 1H), 8.06-8.08 (m, 2H), 7.63-7.65 (m, 2H), 7.48-7.57 (m, 3H), 7.34-7.36 (m, 3H), 3.85-4.01 (m, 4H), 3.33 (d, *J* = 22.8 Hz, 2H), 1.13 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 147.5 (d, *J*(C,P) = 9.9 Hz), 138.8, 136.3 (d, *J*(C,P) = 3.7 Hz), 132.9, 130.0, 128.7, 128.5, 128.3, 126.5, 63.4 (d, *J*(C,P) = 6.6 Hz), 28.2 (d, *J*(C,P) = 134.8 Hz), 16.2 (d, *J*(C,P) = 5.8 Hz). ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 24.3. HRMS (ESI) m/z: calcd. For $C_{17}H_{24}O_6P$ $[M+H]^+$: 355.1306, found: 355.1301.

***Ethyl 3-(diethoxyphosphoryl)-2-methylene-4-oxo-4-phenylbutanoate (12b)*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **12b** (53.2 mg, 0.150 mmol, 75%) as a yellow oil.[22] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 8.01-8.02 (m, 2H), 7.44-7.57 (m, 3H), δ 6.57 (t, *J* = 4.4 Hz, 1H), 6.34 (t, *J* = 4.0 Hz, 1H), 5.68 (d, *J* = 26.0 Hz, 1H), 4.06-4.30 (m, 6H), 1.20-1.33 (m, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 193.3 (d, *J*(C,P) = 5.1 Hz), 165.9 (d, *J*(C,P) = 7.0 Hz), 136.2 (d, *J*(C,P) = 4.1 Hz), 133.6, 131.2 (d, *J*(C,P) = 8.5 Hz), 131.0 (d, *J*(C,P) = 8.0 Hz), 129.0, 128.7, 63.1 (dd, *J*(C,P) = 6.5 Hz, 41.1 Hz), 61.8, 47.0 (d, *J*(C,P) = 137.3 Hz), 16.3 (dd, *J*(C,P) = 6.2 Hz, 10.0 Hz), 14.2. ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 19.2.

***Diethyl (2-(4-ethylphenyl)-2-oxoethyl)phosphonate (6a')*:** According to the general procedure, work-up and flash column chromatography (Hexane/EtOAc: 1:1) gave product **6a'** (48.9 mg, 0.172 mmol, 86%) as a pale yellow oil.[10a] ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 7.93-7.95 (m, 2H), 7.29-7.31 (m, 2H), 4.10-4.18 (m, 4H), 3.62 (d, *J* = 22.8 Hz, 2H), 2.68-2.74 (m, 2H), 1.26-1.36 (m, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 191.6 (d, *J*(C,P) = 6.4 Hz), 150.8, 134.3 (d, *J*(C,P) = 1.8 Hz), 129.3, 128.2, 62.7 (d, *J*(C,P) = 6.5 Hz), 38.4, 28.2 (d, *J*(C,P) = 129.4 Hz), 16.3 (d, *J*(C,P) = 6.3 Hz), 15.1. ^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ^{o}C, TMS): δ = 20.3.

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ASSOCIATED CONTENT:

• Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

• Supporting Information Statement

Copies of ^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

FAIR Data is available as Supporting Information for Publication and includes the primary NMR FID files for compounds [**3a**-**ad**, **4a**-**t**, **6a'**, **10a**, **12a**-**b**].

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