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# Mn(acac)$_3$ 促进烯醇酯与亚磷酸酯的自由基氧化偶联反应合成 β-酮膦酸酯

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**摘要** β-酮膦酸酯作为在天然产物和生物活性分子中广泛存在的结构骨架, 在药物化学和有机转化等领域具有重要的合成价值. 报道了一种 Mn(acac)$_3$ 促进的芳基烯醇酯酸酯和烷基亚磷酸酯的氧化偶联反应, 在温和且简单的条件下, 实现了具有广泛官能团兼容性的 β-酮膦酸酯的合成. 反应步骤中涉及了锰氧化的膦自由基的生成以及自由基对不饱和键的加成过程. 反应中所需的底物方便易得, 且体系不需要任何酸或碱作为添加剂. 最后进行了克级放大实验, 进一步证明了这一策略在高效合成 β-酮膦酸酯中的价值.

**关键词** β-酮膦酸酯; 自由基加成; 氧化偶联

# Mn(acac)$_3$ Promoted Radical Oxidative Coupling Reaction of Enol Esters with Phosphites to Synthesize β-Ketophosphonates

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**Abstract** β-Ketophosphonates are widely found in the structural backbone of natural products and biologically active molecules, and they are of great synthetic value in medicinal chemistry, organic transformations and other fields. An Mn(acac)$_3$-promoted oxidative coupling reaction between aryl enol acetates and alkyl phosphites are reported, enabling the synthesis of β-ketophosphonates with broad functional group compatibility under mild and simple conditions. The generation of phosphorus radicals for manganese oxidation and the addition of radicals to unsaturated bonds were involved in the reaction. The substrates required for the reaction were readily available and the system did not require any acid or base as additives. Finally, a gram-scale experiment to further demonstrate the value of this strategy in the efficient synthesis of β-ketophosphonates was carried out.

**Keywords** β-ketophosphonates; radical addition; oxidative coupling

## 1 Introduction

As one of the most important classes of organophosphorus compounds, β-ketophosphonates are widely present in various natural products, pharmaceuticals and functional materials.[1] And it is also used in medicinal chemistry owing to their biological activity.[2] Considering the value in synthesis, many efforts have been made for the synthesis of these compounds.

Traditionally, β-ketophosphonates were usually constructed through the reaction of α-haloketones with trialkylphosphites or the acylation of alkylphosphonates with esters.[3] However, strong bases were often required in these transformations, which limits the application of these strategies. There is still an urgent need to develop more mild and convenient strategies for the synthesis of these compounds. The essence of organic synthetic chemistry is the establishment of different chemical bonds. In recent years, there has been an increasing interest in radical reactions that build new chemical bonds through unique reaction pipelines.[4] And this strategy has also been applied to the construction of carbon-phosphorus bonds. In 2015, Lei's groups[5] developed a radical-radical cross coupling reaction for the synthesis of β-ketophosphonates, and two different radicals were obtained at the same times by using an internal oxidant. On the other hand, unsaturated bonds were often used as effective trapping agents for free radicals to achieve the construction of carbon-carbon,[6] carbon-nitrogen,[7] carbon-sulfur,[8] carbon-silicon bonds.[9] And several elegant reports also described the oxidative addition of phosphine radicals with alkenes or alkynes to form carbon-phosphorus bonds.[10] Besides, Song and Yu's

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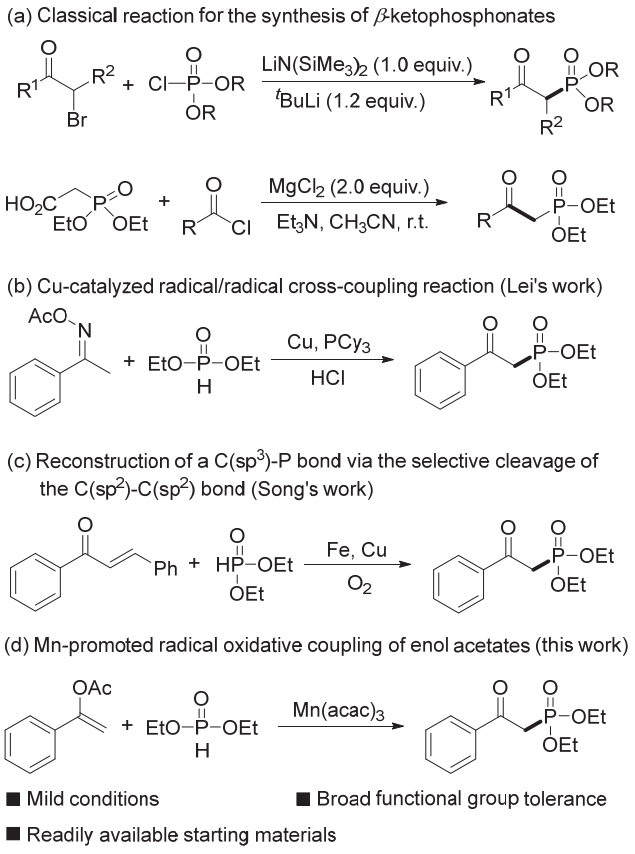
groups[11] also described the regioselective C($sp^2$)—C($sp^2$) bond cleavage and C($sp^3$)—P bond formation, respectively, which involved phosphorus radical attack on double bonds and C—C (C=O) bond cleavage. As a class of electron-deficient olefins, silyl enol ethers and enol acetates usually serve as platforms to synthesize functionalized ketones through the attraction of electrophilic radical species.[12] Herein, based on our interest in developing more efficient strategy for the synthesis of *β*-ketophosphonates, we developed a manganese-promoted oxidative coupling of enol acetates to synthesize these compounds. The formation of carbon-phosphorus bonds and the capture of phosphorus radicals by unsaturated bonds could be achieved under mild conditions and without the need of any base or acid. And various *β*-ketophosphonates were obtained in moderate to good yields.




**Scheme 1** Synthetic strategies of *β*-ketophosphonates

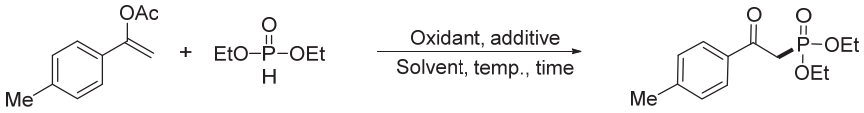
## 2 Results and discussion

At the beginning of the study, enol acetate **1a** and diethyl phosphite **2a** were used in model reaction. As shown in Table 1, using 1.5 equiv. of $Mn(acac)_3$ as oxidant and $CH_3CN$ as solvent in the air atmosphere, the target product **3a** was obtained in 55% yield at 80 ℃ for 6 h (Table 1, Entry 1). Then several manganese metal salts and commonly used oxidants were examined, and almost no product was obtained except for $Mn(acac)_2$, which gave a yield of 32% (Table 1, Entries 2～8). We also tried using catalytic amounts of $Mn(acac)_3$ in combination with 1.5 equiv. of oxidants such as DTBP or $K_2S_2O_8$, but did not obtain any product (Table 1, Entries 9～10). Subsequently, various solvents were tested in the reaction system, and most of them (except NMP) could deliver the product, but there was no increase in the yield (Table 1, Entries 11～16). The amounts of oxidant and substrate were also adjusted. When 2.0 equiv. of $Mn(acac)_3$ were used instead of 1.5 equiv., the yield of the product was improved to 70% (Table 1, Entry 17). When 3.0 equiv. of $Mn(acac)_3$ were used in the reaction, fortunately, the yield increased to 81% (Table 1, Entry 18). The amount of $Mn(acac)_3$ further increased to 4.0 equiv., the yield decreased (Table 1, Entry 19). When the amount of diethyl phosphite **2a** was reduced to 1.5 equiv., there has been a slight decrease in yield, and increasing the amount of diethyl phosphite to 4.0 equiv. only gave a slight increase in yield (from 74% to 85%), so 2.0 equiv. of diethyl phosphite was chosen for subsequent optimization (Table 1, Entries 20, 21). Various bases or acids have been used as additives to add into the system, but they all showed a inhibitory effect on the reaction (Table 1, Entries 22～25). This may be due to the decomposition of the enol acetates to aryl ketones under acidic or basic conditions. Besides, either increasing or decreasing the temperature had a negative effect on the reaction, and adjusting the reaction time did not give a better result (Table 1, Entries 26～29). When the reaction was carried out at $N_2$ atmosphere, 82% yield was still obtained, which ruled out the possibility of oxygen influencing the reaction (Table 1, Entry 30). Finally, the desired product **3a** was obtained in 81% yield by reacting 0.5 mmol of **1a** with 2.0 equiv. of diethyl phosphite **2a** in the presence of 3.0 equiv. of $Mn(acac)_3$ in $CH_3CN$ (5.0 mL) at 80 ℃ for 6 h under air atmosphere.

With the optimized conditions in hand, the scope of substrates in the reaction was examined. First, aryl enol acetates with different substituents on the benzene ring were tested and the results were presented in Table 2. When no substituent was present on the benzene, 84% yield of the corresponding product **3b** was obtained. Substrates with electron-donating groups on the benzene rings, such as alkyl (**3c**～**3d**), phenyl (**3e**), methoxy (**3f**), phenoxy (**3g**), benzyloxy (**3h**), all gave the desired products in good yields (60%～80%). The aryl enol acetates substituted with electron-withdrawing groups could also convert smoothly to give the corresponding product in excellent yields, and the presence of bromine and iodine atoms provided the potential for subsequent structural modifications (**3i**～**3k**). Unfortunately, the reaction could not occur when a strong electron-absorbing nitro group was attached to the benzene ring (**3l**). In addition, both *ortho*-, and *meta*-substituted aryl enol acetates were converted into the target product smoothly (**3m**～**3o**). When there were multiple substituted groups on the benzene ring, the corresponding products were still obtained in medium to upper yields (**3p**～**3q**). Replacement of the benzene ring with naphthalene and thiophene rings gave products **3r** and **3s**

**Table 1** Optimization of the reaction conditions




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

| Entry | Oxidant (equiv.) | Additive (equiv.) | Solvent | Temp./℃ | Time/h | Yield[b]/% |
|---|---|---|---|---|---|---|
| 1 | $Mn(acac)_3$ (1.5) | | $CH_3CN$ | 80 | 6 | 55 |
| 2 | $Mn(OAc)_3$ (1.5) | | $CH_3CN$ | 80 | 6 | Trace |
| 3 | $Mn(acac)_2$ (1.5) | | $CH_3CN$ | 80 | 6 | 32 |
| 4 | $K_2S_2O_8$ (1.5) | | $CH_3CN$ | 80 | 6 | ND[f] |
| 5 | $NH_4S_2O_8$ (1.5) | | $CH_3CN$ | 80 | 6 | ND[f] |
| 6 | DTBP (1.5) | | $CH_3CN$ | 80 | 6 | ND[f] |
| 7 | TBHP (1.5) | | $CH_3CN$ | 80 | 6 | ND[f] |
| 8 | $H_2O_2$ (1.5) | | $CH_3CN$ | 80 | 6 | Trace |
| 9 | $Mn(acac)_3$ (0.2)＋DTBP (1.5) | | $CH_3CN$ | 80 | 6 | Trace |
| 10 | $Mn(acac)_3$ (0.2)＋$K_2S_2O_8$ (1.5) | | $CH_3CN$ | 80 | 6 | ND[f] |
| 11 | $Mn(acac)_3$ (1.5) | | 1,4-Dioxane | 80 | 6 | 46 |
| 12 | $Mn(acac)_3$ (1.5) | | THF | 80 | 6 | 38 |
| 13 | $Mn(acac)_3$ (1.5) | | DCE | 80 | 6 | 43 |
| 14 | $Mn(acac)_3$ (1.5) | | EA | 80 | 6 | 58 |
| 15 | $Mn(acac)_3$ (1.5) | | DMF | 80 | 6 | 32 |
| 16 | $Mn(acac)_3$ (1.5) | | NMP | 80 | 6 | Trace |
| 17 | $Mn(acac)_3$ (2.0) | | $CH_3CN$ | 80 | 6 | 70 |
| 18 | $Mn(acac)_3$ (3.0) | | $CH_3CN$ | 80 | 6 | 81 |
| 19 | $Mn(acac)_3$ (4.0) | | $CH_3CN$ | 80 | 6 | 72 |
| 20 | $Mn(acac)_3$ (3.0) | | $CH_3CN$ | 80 | 6 | 74[c] |
| 21 | $Mn(acac)_3$ (3.0) | | $CH_3CN$ | 80 | 6 | 85[d] |
| 22 | $Mn(acac)_3$ (3.0) | $CH_3CO_2H$ (2.0) | $CH_3CN$ | 80 | 6 | 51 |
| 23 | $Mn(acac)_3$ (3.0) | $C_4H_9CO_2H$ (2.0) | $CH_3CN$ | 80 | 6 | 56 |
| 24 | $Mn(acac)_3$ (3.0) | $NEt_3$ (2.0) | $CH_3CN$ | 80 | 6 | 61 |
| 25 | $Mn(acac)_3$ (3.0) | DBU (2.0) | $CH_3CN$ | 80 | 6 | 48 |
| 26 | $Mn(acac)_3$ (3.0) | — | $CH_3CN$ | 60 | 6 | 72 |
| 27 | $Mn(acac)_3$ (3.0) | — | $CH_3CN$ | 100 | 6 | 66 |
| 28 | $Mn(acac)_3$ (3.0) | — | $CH_3CN$ | 80 | 4 | 69 |
| 29 | $Mn(acac)_3$ (3.0) | — | $CH_3CN$ | 80 | 8 | 79 |
| 30[e] | $Mn(acac)_3$ (3.0) | — | $CH_3CN$ | 80 | 6 | 82[e] |

[a] **1a** (0.5 mmol), **2a** (1.0 mmol, 2.0 equiv.), $Mn(acac)_3$ (1.5 mmol, 3.0 equiv.), 80 ℃, 6 h, $CH_3CN$ (5 mL), under air atmosphere. [b] Isolated yield. [c] **1a**∶**2a**=1∶1.5. [d] **1a**∶**2a**=1∶3. [e] $N_2$ atmosphere. [f] ND=no detected. DBU=1,8-diazabicyclo[5.4.0]undec-7-ene.

in 77% and 56% yields, respectively. When the diethyl phosphite was replaced with dimethyl phosphite and diphenylphosphine oxide, the desired product **3t** was obtained in 85% yield, but product **3u** can't harvest.

Subsequently, in order to illustrate the potential value of this reaction, the gram-scale reaction under standard conditions was finished. As shown in Scheme 2, 7 mmol of **1a** and 14 mmol of **2a** were used as the starting substrates, and the reaction was carried out at standard conditions. After separation of the products, 1.38 g of *β*-ketophosphonates **3a** was obtained in 73% yield.

For a better mechanistic understanding, several radical-trapping experiments were carried out. As shown in Scheme 3, when 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 3.0 equiv.) or 2,6-ditertbutyl-4-methylphenol (BHT, 2.0 equiv.) was added as a radical capture agent to the reaction under standard conditions, the reaction was completely inhibited and no product was detected. These results suggested that a radical pathway might be involved in the reaction.

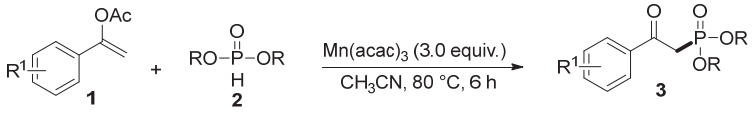
Based on previous literature,[13-14] a plausible mechanism for this reaction was proposed. Firstly, diethyl phosphite **2a** was isomerized to trivalent phosphine species, which was then oxidized by $Mn^{3+}$ to give a phosphorus radical **A**. Then **A** was captured by unsaturated bonds to form another carbon radical **B**, and **B** was further oxidized by $Mn^{3+}$ to give intermediate **C**. Finally, intermediate **C** was followed by hydrolysis[15] and the target product **3a** was obtained in the reaction system.

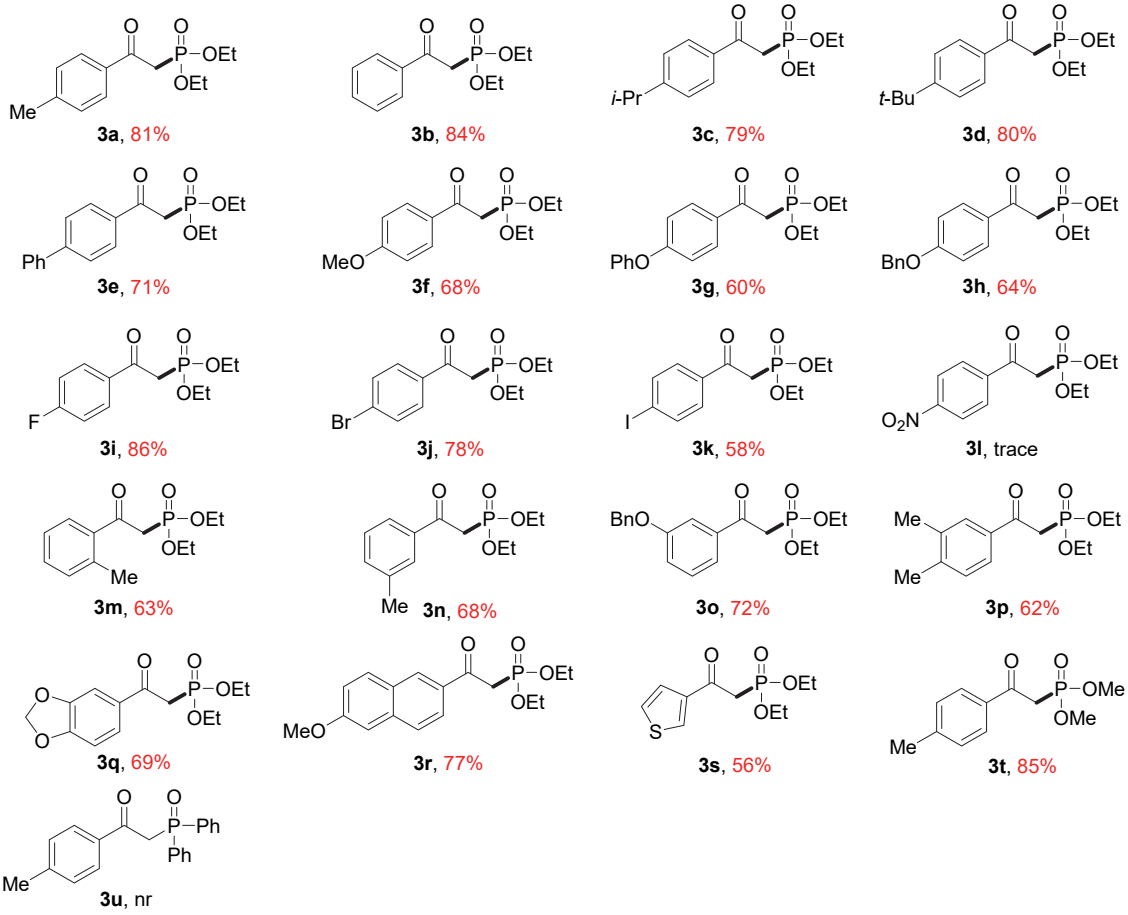
## 3 Conclusions

In summary, we have developed a manganese-promoted radical oxidative coupling reaction for the synthesis of

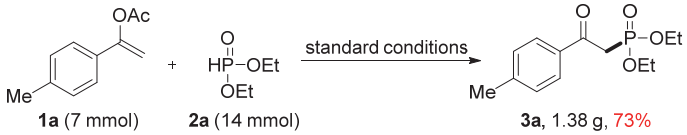
  

**Table 2** Scope of substrates for the synthesis of **3a**～**3u**[a]

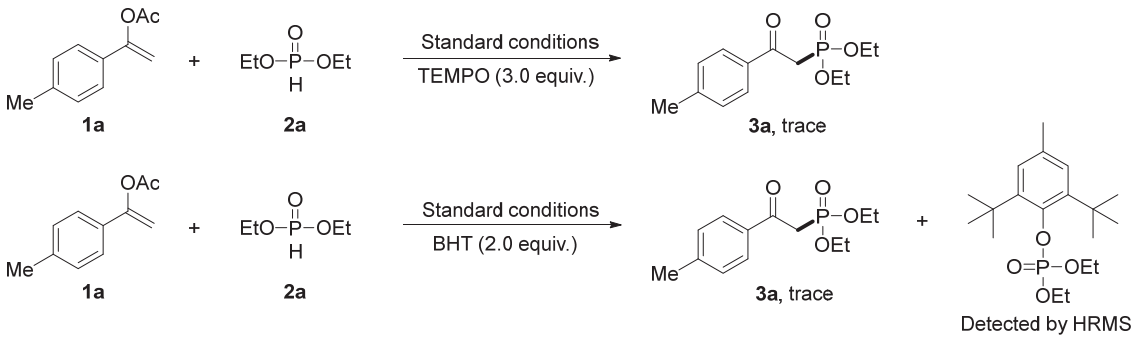



[a] Reaction conditions: **1** (0.5 mmol, 1.0 equiv.), **2** (1.0 mmol, 2.0 equiv.), $Mn(acac)_3$ (1.5 mmol, 3.0 equiv.), 80 ℃, 6 h, $CH_3CN$ (5 mL), under air atmosphere. Isolated yield. nr, no reaction.

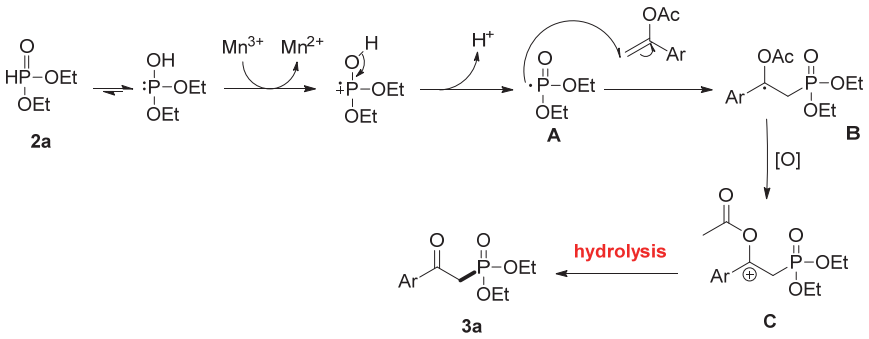



**Scheme 2** Gram-scale reaction of **3a**




**Scheme 3** Radical-trapping experiments




**Scheme 4** Proposed mechanism of reaction

*β*-ketophosphonates under mild conditions. In this reaction, the phosphorus radical was generated by the oxidation of manganese metal salts, and conveniently available enol esters were used as radical trapping agents and platforms for ketone production. Various *β*-ketophosphonates were delivered in moderate to good yields. The reaction showed good functional group tolerance under simple and mild conditions that may be regarded as a good method for the preparation of *β*-ketophosphonates. Finally, we proposed a possible mechanism for the reaction.

## 4 Experimental section

### 4.1 Instruments and reagents

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All reactions were carried out in air atmosphere and monitored by TLC (thin layer chromatography). The products were purified by column chromatography using 200～300 mesh silica. The elution solvent used for column chromatography was PE (petroleum ether, boiling point range 60～90 ℃), EA (ethyl acetate) and DCM (dichloromethane). The $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectroscopic analyses were carried out on a Bruker AV spectrometer. $^1$H NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts ($\delta$) were reported from the resonance of tetramethyl silane as the internal standard (TMS: $\delta$ 0.00). $^{13}$C NMR spectra were recorded on 100 with complete proton decoupling spectrophotometers.

### 4.2 General procedure for synthesis of enol acetates **1**

A 100 mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser was charged with ketone (50 mmol, 1.0 equiv.), isopropenyl acetate (250 mmol, 5.0 equiv.) and *p*-TsOH (4 mmol, 0.08 equiv.). The reaction mixture was heated to 120 ℃ in aluminum dry block heater. After 24 h, the reaction mixture was allowed to cool to room temperature and the remaining isopropenyl acetate was subsequently evaporated under reduced pressure. The residue was redissolved in ethyl acetate (100 mL), washed with $H_2O$ (150 mL) and dried over $Na_2SO_4$. The solvent was evaporated *in vacuo* to give a dark red oil. The pure products were obtained by distillation under reduced pressure or by purification on $SiO_2$ column chromatography (PE/DCM, *V*/*V*=1/1). All enol acetates (**1a**～**1s**) were synthesized and purified according to the above procedure and in agreement with reference.[16]

### 4.3 Synthesis of product **3**

A 25 mL round bottom flask was charged with aryl enol acetates **1** (0.5 mmol, 1.0 equiv.), diethyl phosphite **2** (1.0 mmol, 2.0 equiv.), $Mn(acac)_3$ (1.5 mmol, 3.0 equiv.), acetonitrile (5 mL) and a magnetic stir bar under air atmosphere. The reaction mixture was stirred and reacted at 80 ℃ for 6 h. The reaction was basically completed. The mixture was poured into water (15 mL) and extracted with ethyl acetate (10 mL×3). The combined organic layer was dried over $MgSO_4$ and evaporated to give the crude product, which was then purified on silica gel (PE/EA, *V*/*V*=2/1～1/1) to afford target compounds **3** as a yellow oily liquid.

Diethyl(2-(1-(4-phenoxyphenyl))-2-oxoethyl)phosphonate (**3a**):[17a] 1-(4-Phenoxyphenyl)vinyl acetate (88.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3a** as light yellow oil liquid (109.3 mg, 81%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.92 (d, *J*=8.0 Hz, 2H), 7.28 (d, *J*=8.0 Hz, 2H), 4.18～4.11 (m, 4H), 3.62 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 2.42 (s, 3H), 1.29 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.5 (d, $J_{C\text{-}P}$=7.0 Hz), 144.6, 134.1, 129.3, 62.6 (d, $J_{C\text{-}P}$=7.0 Hz), 38.3 (d, $J_{C\text{-}P}$=129.0 Hz), 21.6, 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.4.

Diethyl(2-(1-phenyl)-2-oxoethyl)phosphonate (**3b**):[17a] 1-Phenylvinyl acetate (81.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3b** as yellow oil liquid (107.5 mg, 84%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.95 (d, *J*=8.0 Hz, 2H), 7.52 (t, *J*=6.0 Hz, 1H), 7.41 (t, *J*=8.0 Hz, 2H), 4.11～4.03 (m, 4H), 3.57 (d, $J_{H\text{-}P}$=12.0 Hz, 2H), 1.21 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.9 (d, $J_{C\text{-}P}$=6.0 Hz), 136.5, 133.6, 129.0, 128.6, 62.6 (d, $J_{C\text{-}P}$=6.0 Hz), 38.5 (d, $J_{C\text{-}P}$=129.0 Hz), 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.2.

Diethyl(2-(1-(4-(iso-propyl)phenyl))-2-oxoethyl)phos-

phonate (**3c**):[17b] 1-(4-(*iso*-Propyl)phenyl)vinyl acetate (102.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3c** as light yellow oil liquid (117.7 mg, 79%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.96 (d, *J*=8.0 Hz, 2H), 7.34 (d, *J*=8.0 Hz, 2H), 4.19～4.12 (m, 4H), 3.63 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 3.02～2.95 (m, 1H), 1.31 (d, *J*=4.0 Hz, 6H), 1.28 (t, *J*=16.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.5 (d, $J_{C\text{-}P}$=6.0 Hz), 155.3, 134.4, 129.4, 126.7, 62.7 (d, $J_{C\text{-}P}$=6.0 Hz), 38.4 (d, $J_{C\text{-}P}$=130.0 Hz), 34.3, 23.6, 16.3 (d, $J_{C\text{-}P}$=7.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.4.

Diethyl(2-(1-(4-(tert-butyl)phenyl))-2-oxoethyl)phosphonate (**3d**):[17a] 1-(4-(*tert*-Butyl)phenyl)vinyl acetate (109.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3d** as light yellow oil liquid (124.8 mg, 80%); $R_f$=0.3 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.97 (d, *J*=8.0 Hz, 2H), 7.50 (d, *J*=8.0 Hz, 2H), 4.19～4.13 (m, 4H), 3.63 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.35 (s, 9H), 1.30 (t, *J*=16.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.5 (d, $J_{C\text{-}P}$=6.0 Hz), 157.5, 134.0, 129.1, 125.6, 62.7 (d, $J_{C\text{-}P}$=6.0 Hz), 38.4 (d, $J_{C\text{-}P}$=129.0 Hz), 35.2, 31.0, 16.3 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.3.

Diethyl(2-(1-([1,1'-biphenyl]-4-yl))-2-oxoethyl)phosphonate (**3e**):[16d] 1-([1,1'-Biphenyl]-4-yl)vinyl acetate (119.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3e** as yellow liquid (117.9 mg, 71%); $R_f$=0.3 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.11 (d, *J*=8.0 Hz, 2H), 7.72 (d, *J*=8.0 Hz, 2H), 7.65 (d, *J*=8.0 Hz, 2H), 7.50 (t, *J*=8.0 Hz, 2H), 7.43 (t, *J*=8.0 Hz, 1H), 4.22～4.15 (m, 4H), 3.69 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.32 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.5 (d, $J_{C\text{-}P}$=6.0 Hz), 146.4, 139.7, 135.2, 129.7, 128.9, 128.4, 127.3, 127.2, 62.8 (d, $J_{C\text{-}P}$=7.0 Hz), 38.6 (d, $J_{C\text{-}P}$=129.0 Hz), 16.3 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 21.3.

Diethyl(2-(1-(4-methoxyphenyl))-2-oxoethyl)phosphonate (**3f**):[17a] 1-(4-Methoxyphenyl)vinyl acetate (96.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3f** as light yellow oil liquid (97.2 mg, 68%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.00 (d, *J*=8.0 Hz, 2H), 6.95 (d, *J*=8.0 Hz, 2H), 4.17～4.10 (m, 4H), 3.88 (s, 3H), 3.59 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.29 (t, *J*=16.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 190.2 (d, $J_{C\text{-}P}$=6.0 Hz), 163.9, 129.5, 113.7, 62.5 (d, $J_{C\text{-}P}$=7.0 Hz), 55.5, 38.1 (d, $J_{C\text{-}P}$=129.0 Hz), 16.2 (d, $J_{C\text{-}P}$=7.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.8.

Diethyl(2-(1-(4-phenoxyphenyl))-2-oxoethyl)phosphonate (**3g**):[17d] 1-(4-Phenoxyphenyl)vinyl acetate (127.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3g** as light yellow oil liquid (104.4 mg, 60%); $R_f$=0.3 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.02 (d, *J*=8.0 Hz, 2H), 7.42 (t, *J*=8.0 Hz, 2H), 7.23 (t, *J*=8.0 Hz, 1H), 7.09 (d, *J*=8.0 Hz, 2H), 7.02 (d, *J*=8.0 Hz, 1H), 4.20～4.13 (m, 4H), 3.61 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.31 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 190.3 (d, $J_{C\text{-}P}$=7.0 Hz), 162.6, 155.2, 131.5, 131.1, 130.1, 120.4, 117.1, 62.8 (d, $J_{C\text{-}P}$=7.0 Hz), 38.4 (d, $J_{C\text{-}P}$=129.0 Hz), 16.3 (d, $J_{C\text{-}P}$=7.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.0.

Diethyl(2-(1-(4-(benzyloxy)phenyl))-2-oxoethyl)phosphonate (**3h**):[17d] 1-(4-(Benzyloxy)phenyl)vinyl acetate (134.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3h** as light yellow oil liquid (115.8 mg, 64%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.01 (d, *J*=8.0 Hz, 2H), 7.44～7.36 (m, 5H), 7.04 (d, *J*=8.0 Hz, 2H), 5.15 (s, 2H), 4.19～4.12 (m, 4H), 3.60 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.30 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 190.3 (d, $J_{C\text{-}P}$=6.0 Hz), 163.1, 136.0, 131.6, 129.8, 128.7, 128.3, 127.5, 114.6, 70.2, 62.7 (d, $J_{C\text{-}P}$=7.0 Hz), 38.2 (d, $J_{C\text{-}P}$=129.0 Hz), 16.3 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 19.9.

Diethyl(2-(1-(4-fluorophenyl))-2-oxoethyl)phosphonate (**3i**):[17a] 1-(4-Fluorophenyl)vinyl acetate (90.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3i** as light yellow oil liquid (117.8 mg, 86%); $R_f$=0.3 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.99 (q, *J*=8.0 Hz, 2H), 7.08 (t, *J*=8.0 Hz, 2H), 4.11～4.03 (m, 4H), 3.54 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.22 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 190.3 (d, $J_{C\text{-}P}$=6.0 Hz), 167.3, 164.8, 132.9, 131.9 (d, $J_{C\text{-}F}$=10.0 Hz), 115.7 (d, $J_{C\text{-}F}$=22.0 Hz), 62.7 (d, $J_{C\text{-}P}$=6.0 Hz), 38.7 (d, $J_{C\text{-}P}$=128.0 Hz), 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.2.

Diethyl(2-(1-(4-bromophenyl))-2-oxoethyl)phosphonate (**3j**):[17a] 1-(4-Bromophenyl)vinyl acetate (120.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3j** as light yellow oil liquid (130.2 mg, 78%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.89 (d, *J*=8.0 Hz, 2H), 7.62 (d, *J*=8.0 Hz, 2H), 4.17～4.10 (m, 4H), 3.60 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.29 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.0 (d, $J_{C\text{-}P}$=7.0 Hz), 135.2, 131.9, 130.6, 129.1, 62.8 (d, $J_{C\text{-}P}$=7.0 Hz), 38.2 (d, $J_{C\text{-}P}$=129.0 Hz), 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.1.

Diethyl(2-(1-(4-iodophenyl))-2-oxoethyl)phosphonate (**3k**): 1-(4-Iodophenyl)vinyl acetate (144.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3k** as light yellow liquid (110.7 mg, 58%); $R_f$=0.3 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.86 (d, *J*=8.0 Hz, 2H), 7.73 (d, *J*=12.0 Hz, 2H), 4.18～4.11 (m, 4H), 3.59 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.30 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.2 (d, $J_{C\text{-}P}$=6.0 Hz), 137.9, 135.7, 130.4, 102.0, 62.7 (d, $J_{C\text{-}P}$=7.0 Hz), 38.5 (d, $J_{C\text{-}P}$=129.0 Hz), 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.0; HRMS (ESI) calcd for $C_{12}H_{17}IO_4P$ $[M+H]^+$ 382.9904, found 382.9908.

Diethyl(2-(1-(*o*-tolyl))-2-oxoethyl)phosphonate (**3m**):[17d] 1-(*o*-Tolyl)vinyl acetate (88.0 mg, 0.5 mmol) and

diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3m** as yellow oil liquid (85.0 mg, 63%); $R_f$=0.3 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.68 (d, *J*=8.0 Hz, 1H), 7.32 (t, *J*=16 Hz, 1H), 7.20 (q, *J*=24.0 Hz, 2H), , 4.08～4.01 (m, 4H), 3.52 (d, $J_{H\text{-}P}$=6.0 Hz, 2H), 2.44 (s, 3H), 1.19 (t, *J*=6.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 195.1 (d, $J_{C\text{-}P}$=7.0 Hz), 138.9, 137.2, 131.9, 129.6, 125.6, 62.5 (d, $J_{C\text{-}P}$=6.0 Hz), 41.0 (d, $J_{C\text{-}P}$=129.0 Hz), 21.3, 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 21.2.

Diethyl(2-(1-(*m*-tolyl))-2-oxoethyl)phosphonate (**3n**):[17d] 1-(*m*-Tolyl)vinyl acetate (88.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3n** as yellow oil liquid (91.8 mg, 68%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.74 (d, *J*=8.0 Hz, 2H), 7.34～7.27 (m, 2H), 4.11～4.03 (m, 4H), 3.56 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 2.34 (s, 3H), 1.21 (t, *J*=6.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 192.1 (d, $J_{C\text{-}P}$=7.0 Hz), 138.4, 136.5, 134.4, 129.4, 128.4, 126.3, 62.6 (d, $J_{C\text{-}P}$=5.0 Hz), 38.5 (d, $J_{C\text{-}P}$=129.0 Hz), 21.3, 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.4.

Diethyl(2-(1-(3-(benzyloxy)phenyl))-2-oxoethyl)phosphonate (**3o**): 1-(3-(Benzyloxy)phenyl)vinyl acetate (134.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3o** as yellow oil liquid (132.1 mg, 72%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.53 (d, *J*=12.0 Hz, 2H), 7.37～7.25 (m, 6H), 7.12 (dd, *J*=4.0, 8.0 Hz, 1H), 5.04 (s, 2H), 4.10～4.02 (m, 4H), 3.53 (d, $J_{H\text{-}P}$=6.0 Hz, 2H), 1.21 (t, *J*=6.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.7 (d, $J_{C\text{-}P}$=7.0 Hz), 158.9, 137.9, 136.4, 129.6, 128.6, 128.1, 127.5, 122.1, 121.1, 114.0, 70.2, 62.6 (d, $J_{C\text{-}P}$=6.0 Hz), 38.6 (d, $J_{C\text{-}P}$=129.0 Hz), 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.2; HRMS (ESI) calcd for $C_{19}H_{24}O_5P$ $[M+H]^+$ 363.1356, found 363.1352.

Diethyl(2-(1-(3,4-(dimethyl)phenyl))-2-oxoethyl)phosphonate (**3p**): 1-(3,4-(Dimethyl)phenyl)vinyl acetate (95.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3p** as yellow oil liquid (88.0 mg, 62%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.77 (t, *J*=10.0 Hz, 2H), 7.23 (d, *J*=4.0 Hz, 1H), 4.18～4.11 (m, 4H), 3.61 (d, $J_{H\text{-}P}$=20.0 Hz, 2H), 1.29 (t, *J*=6.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.7 (d, $J_{C\text{-}P}$=6.0 Hz), 143.4, 136.9, 134.4, 130.0, 129.8, 126.9, 62.6 (d, $J_{C\text{-}P}$=6.0 Hz), 38.3 (d, $J_{C\text{-}P}$=130.0 Hz), 20.0, 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.1; HRMS (ESI) calcd for $C_{14}H_{22}O_4P$ $[M+H]^+$ 285.1250, found 285.1251.

Diethyl(2-(1-(benzo[*d*][1,3]dioxol-5-yl))-2-oxoethyl)-phosphonate (**3q**):[17c] 1-(Benzo[*d*][1,3]dioxol-5-yl)vinyl acetate (103.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3q** as yellow oil liquid (103.5 mg, 69%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.61 (dd, *J*=4.0, 8.0 Hz, 1H), 7.45 (d, *J*=4.0 Hz, 1H), 6.85 (d, *J*=8.0 Hz, 1H), 6.04 (s, 3H), 4.16～4.09 (m, 4H), 3.55 (d, $J_{H\text{-}P}$=28.0 Hz, 2H), 1.19 (t, *J*=6.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 189.8 (d, $J_{C\text{-}P}$=6.0 Hz), 152.4, 148.3, 131.4, 126.1, 108.4, 107.8, 102.0, 62.6 (d, $J_{C\text{-}P}$=7.0 Hz), 38.4 (d, $J_{C\text{-}P}$=129.0 Hz), 16.3 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 19.8.

Diethyl(2-(1-(6-methoxynaphthalen-2-yl))-2-oxoethyl)-phosphonate (**3r**): 1-(6-Methoxynaphthalen-2-yl)vinyl acetate (121.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3r** as yellow oil liquid (129.4 mg, 77%); $R_f$=0.3 (PE/EA, *V*/*V*=2/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.49 (s, 1H), 8.04 (dd, *J*=2.0, 8.0 Hz, 1H), 7.89 (d, *J*=12.0 Hz, 1H), 7.78 (d, *J*=8.0 Hz, 1H), 7.22 (dd, *J*=2.8, 12.0 Hz, 1H), 7.17 (d, *J*=4.0 Hz, 1H), 4.20～4.13 (m, 4H), 3.96 (s, 3H), 3.75 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.29 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.4 (d, $J_{C\text{-}P}$=6.0 Hz), 160.1, 137.6, 132.0, 131.4, 127.7, 127.2, 124.9, 119.9, 62.7 (d, $J_{C\text{-}P}$=7.0 Hz), 55.4, 38.3 (d, $J_{C\text{-}P}$=129.0 Hz), 16.3 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 19.8; HRMS (ESI) calcd for $C_{17}H_{22}O_5P$ $[M+H]^+$ 337.1199, found 337.1195.

Diethyl(2-(1-(thiophen-3-yl))-2-oxoethyl)phosphonate (**3s**):[17d] 1-(Thiophen-3-yl)vinyl acetate (84.0 mg, 0.5 mmol) and diethyl phosphite (138.1 mg, 1.0 mmol) were used to afford the title compound **3s** as yellow oil liquid (73.3 mg, 56%); $R_f$=0.2 (PE/EA, *V*/*V*=1/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.15 (m, 1H), 7.50 (d, *J*=4.0 Hz, 1H), 7.26～7.23 (m, 1H), 4.10～4.03 (m, 4H), 3.46 (d, $J_{H\text{-}P}$=24.0 Hz, 2H), 1.22 (t, *J*=8.0 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 185.6 (d, $J_{C\text{-}P}$=7.0 Hz), 141.8, 134.3, 127.2, 126.4, 62.7 (d, $J_{C\text{-}P}$=6.0 Hz), 40.0 (d, $J_{C\text{-}P}$=128.0 Hz), 16.2 (d, $J_{C\text{-}P}$=6.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 19.3.

Dimethyl(2-(1-(4-phenoxyphenyl))-2-oxoethyl)phosphonate (**3t**):[17e] 1-(4-Phenoxyphenyl)vinyl acetate (88.0 mg, 0.5 mmol) and dimethyl phosphite (110.0 mg, 1.0 mmol) were used to afford the title compound **3t** as yellow oil liquid (102.8 mg, 85%); $R_f$=0.2 (PE/EA, *V*/*V*=2/1). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 7.83 (d, *J*=8.0 Hz, 2H), 7.21 (d, *J*=8.0 Hz, 2H), 3.70 (d, *J*=6.0 Hz, 6H), 3.55 (d, $J_{H\text{-}P}$=20.0 Hz, 2H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$: 191.3 (d, $J_{C\text{-}P}$=6.0 Hz), 144.8, 133.9, 129.4, 129.1, 53.1 (d, $J_{C\text{-}P}$=6.0 Hz), 37.4 (d, $J_{C\text{-}P}$=131.0 Hz), 23.3; $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$: 20.3.

**Supporting Information** General procedures for gram-scale reaction and radical-trapping experiments, and $^1$H NMR, $^{13}$C NMR and $^{31}$P NMR spectra of compounds **3a**～**3t**. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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