Tetrahedron 68 (2012) 6032–6037

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

An efficient synthesis of enol phosphates via organic base-promoted addition of phosphites to 4-oxo-enoates

Xiao-Yu Zhu, Jia-Rong Chen, Liang-Qiu Lu *, Wen-Jing Xiao *

Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei 430079, China

ARTICLE INFO

Article history:
Received 15 January 2012
Received in revised form 27 April 2012
Accepted 4 May 2012
Available online 12 May 2012

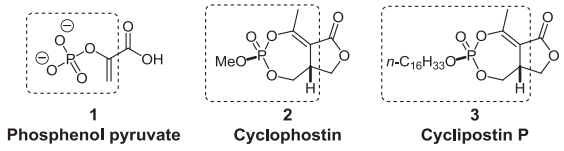
Keywords:
Hydrophosphorylation
4-Oxo-enonate
Enol phosphate
High stereoselectivity

ABSTRACT

A TMG catalyzed, practical and efficient hydrophosphorylation of 4-oxo-enoates by diethyl or diphenyl phosphite has been described. This protocol allows a convenient access to a variety of enol phosphates under mild conditions in good yield with excellent stereoselectivity.

1. Introduction

Enol phosphates are an important class of organophosphates that exhibit a variety of biological properties.[1] For example, phosphenol pyruvate (PEP) **1** is well known high-energy species, which plays an important role in transformation of ADP to ATP (Fig. 1).[2] The natural cyclophostin **2** shows potent inhibition of acetyl cholinesterase (AChE) from the housefly (CSMA strain) and the brown plant hopper. The cyclipostin **3** bearing a long chain lipophilic alcohol is potent inhibitor of hormone sensitive lipase (HSL).[3] Moreover, diversely functionalized enol phosphates are of great synthetic importance due to their versatile synthetic applications.[4] The generally synthetic methods for enol phosphates are based on Perkow reaction of α-haloketones or α-haloaldehydes with trialkyl phosphites or the reaction of enolate anions with dialkyl phosphorochloridates.[5] However, the wide application of these methods are usually impeded by certain issues, such as formation of side product and the selectivity of the corresponding product (kinetic vs thermodynamic). Therefore, the development of new efficient and highly selective strategies for the preparation of enol phosphates is still highly desirable.



1 Phosphenol pyruvate — 2 Cyclophostin — 3 Cyclipostin P

Fig. 1. Examples of biologically active enol phosphate derivatives.

Recently, Lee and co-workers have developed an elegant gold (I) complex catalyzed addition of diphenyl phosphite to alkynes, which afforded a variety of kinetic enol phosphates or the thermodynamically favored enol phosphates in high yield and selectivity by using different ligands.[6] Inspired by this pioneering achievements, we envisioned that proper tuning of the steric hindrance of the reactants and reaction parameters would probably provide another avenue for the synthesis of enol phosphates. As part of our ongoing program on the development of asymmetric conjugate addition reaction,[7] we recently reported a highly enantioselective Michael addition of nitroalkanes to 4-oxo-enoate **4a**.[7a] Based on these success and highly reactive nature of 4-oxo-enoates, we continued to investigate the addition reaction of phosphites to 4-oxo-enoate **4a**, which would provide a new approach to bioactive phosphate derivatives (Scheme 1).[8] However, in sharp contrast to the previous examples of conjugate addition of dialkyl phosphites to β-aroylacrylic acid (Scheme 1, eq. 1),[9] the reactions of diethyl or diphenyl phosphite and 4-oxo-enoates gave rise to the enol phosphates **6** in good yield and stereoselectivity by use of organic base (Scheme 1, eq. 2).

2. Result and discussion

Initially, the addition of diethyl phosphite (**5a**) to (*E*)-4-oxo-4-phenylbut-2-enoate (**4a**) was selected as the test reaction using 30 mol % of DBU (1,8-diazabicycloundec-7-ene) as the catalyst in

* Corresponding authors. E-mail address: wxiao@mail.ccnu.edu.cn (W.-J. Xiao).

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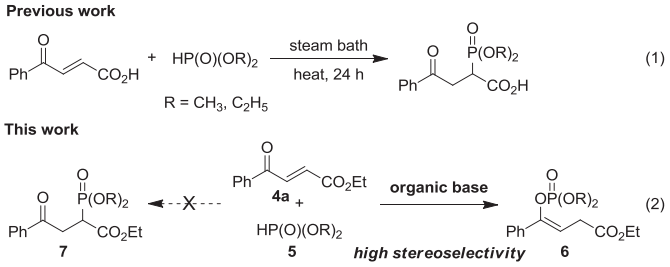
doi:10.1016/j.tet.2012.05.021

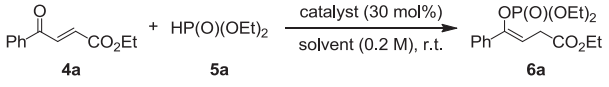


Scheme 1. Strategy for the synthesis of enol phosphates.

toluene at room temperature. Interestingly, the reaction proceeded efficiently and provided the unexpected **6a** as the main product in 56% yield accompanied with a small amount of Michael-type adduct (28% yield) and some other unknown side products (Table 1, entry 1). The structure of **6a** was fully characterized by ^{1}H, ^{13}C, and ^{31}P NMR analysis. Encouraged by these results, we continued to examine other bases for this reaction and found that the bases have great impact on this reaction. For example, the use of commercially available and cheap TMG (1,1,3,3-tetramethylguanidine) resulted in a slight increase of yield while other bases, such as DABCO (1,4-diazabicyclo[2.2.2]octane), pyridine, Et_3N, KOH, and K_2CO_3 led to low yield or even no desired product (entries 3–8). A brief survey of common solvents showed that $CHCl_3$ proved to be the best of choice (entry 12, 64% yield). Moreover, increasing the amount of catalyst to 50 mol % could accelerate the reaction and afford the desired product in 66% yield (entry 18).

With the optimized conditions in hand, we then investigated the scope and limitations of this reaction with a variety of 4-oxo-enoates and phosphites (Table 2). Firstly, we found that this strategy is general with respect to the ester moiety of 4-oxo-enoates (entries 1–4). Changing the ethyl group to methyl, isopropyl, and benzyl groups gave the corresponding products in comparable yields (51–57%). As shown in entries 5–13, the electronic and steric properties of the aromatic ring of 4-oxo-enoates have little impact on the yields. For example, in the case of 4-oxo-enoates bearing

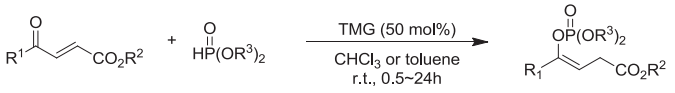
Table 1
Optimization studies[a]

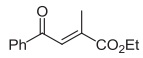


Entry	Solvent	Catalyst	Time (h)	Yield[b] (%)
1	Toluene	DBU[c]	2	56
2	Toluene	TMG[d]	2	58
3	Toluene	DABCO[e]	96	N.R.[f]
4	Toluene	Pyridine	96	N.R.[f]
5	Toluene	Et_3N	96	Trace
6	Toluene	KOH	96	20
7	Toluene	K_2CO_3	96	23
8	DMF	K_2CO_3	2	52
9	Xylene	TMG	2	34
10	CH_2Cl_2	TMG	3	32
11	$Cl(CH_2)_2Cl$	TMG	2	25
12	$CHCl_3$	TMG	20	64
13	Et_2O	TMG	2	51
14	THF	TMG	2	48
15	DMF	TMG	2	43
16	CH_3CN	TMG	2	15
17	C_2H_5OH	TMG	2	46
18[g]	**$CHCl_3$**	**TMG**	**12**	**66**

[a] Reaction conditions: **4a** (0.2 mmol), **5a** (0.4 mmol), catalyst (0.06 mmol), 1 mL solvent, room temperature.
[b] Isolated yield based on **4a**.
[c] DBU=1,8-diazabicycloundec-7-ene.
[d] TMG=1,1,3,3-tetramethylguanidine.
[e] DABCO=1,4-diazabicyclo[2.2.2]octane.
[f] No reaction.
[g] 50 mol % TMG was used.

Table 2
Scope of the 4-oxo-enoates and dialkyl phosphites[a]



Entry	R^1	R^2	**4**	R^3	**6**	Yield[b] (%)
1	Ph	Et	(**4a**)	Et	**6a**	66 (24)
2	Ph	Me	(**4b**)	Et	**6b**	57
3	Ph	^{i}Pr	(**4c**)	Et	**6c**	52
4	Ph	Bn	(**4d**)	Et	**6d**	51
5	*p*-CH_3Ph	Et	(**4e**)	Et	**6e**	53
6	*p*-FPh	Et	(**4f**)	Et	**6f**	62
7	*p*-ClPh	Et	(**4g**)	Et	**6g**	58
8	*p*-BrPh	Et	(**4h**)	Et	**6h**	60
9	*p*-OCH_3Ph	Et	(**4i**)	Et	**6i**	38 (45)
10	*m*-OCH_3Ph	Et	(**4j**)	Et	**6j**	63
11	*m*-ClPh	Et	(**4k**)	Et	**6k**	53
12	*m*-BrPh	Et	(**4l**)	Et	**6l**	71
13	*o*-OCH_3Ph	Et	(**4m**)	Et	**6m**	55
14[c]	Ph	Et	(**4a**)	Ph	**6n**	58
15[d]	Ph	Et	(**4a**)	Ph	**6n**	83
16[d]	*p*-BrPh	Me	(**4n**)	Ph	**6o**	82
17[d]	*p*-NO_2Ph	Et	(**4o**)	Ph	**6p**	54
18[d]	*m*-NO_2Ph	Et	(**4p**)	Ph	**6q**	82
19[d]			(**4q**)	Ph	**6r**	85

[a] Reaction conditions: **4** (0.2 mmol), **5a** (0.4 mmol), TMG (0.1 mmol), 1 mL $CHCl_3$, room temperature, 10~24 h (entries 1–13) or **4** (0.2 mmol), **5b** (0.4 mmol), TMG (0.1 mmol), 2 mL toluene, −20 °C, 0.5~5 h (entries 14–19).
[b] Isolated yield based on **4**. Values in parentheses are the yields of the Michael-type adduct.
[c] Performed in 2 mL toluene at room temperature.
[d] Performed in 2 mL toluene at −20 °C.

CH_3, F, Cl, and Br at the *para*-position of aryl ring, the desired enol phosphates were obtained in good yields (entries 5–8) with the exception of *para*-MeO substituted **4i** (entry 9, 38% yield). Moreover, it was found that the 4-oxo-enoates with electron-withdrawing and donating groups, such as Cl, Br, and MeO at *meta*- and *ortho*- position of phenyl ring also proceeded smoothly to give the products in a range of 53–71% yield (entries 10–13). It was found that toluene is superior to chloroform in the case of diphenyl phosphate and the enol phosphate was obtained in a yield of 58% (entry 14). After brief further screening of the conditions, we found that the reactions of **4a**, **4n**, **4o**, **4p** with diphenyl phosphate can give the corresponding enol phosphate derivatives in satisfying yields in toluene at −20 °C (entries 15–18). It is worth noting that 4-oxo-enoate **4q** with a methyl group at β-carbon can also participate in the reaction to give the desired product in 85% yield after 5 h (entry 19).

Finally, the structure of the enol phosphate **6o** was unambiguously confirmed by X-ray analysis (Fig. 2). Moreover, it was found that the enol phosphate **6o** has *cis*-configuration.[10]

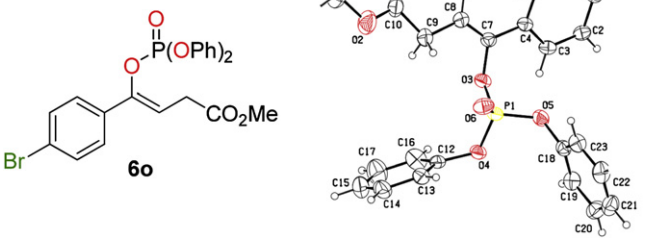
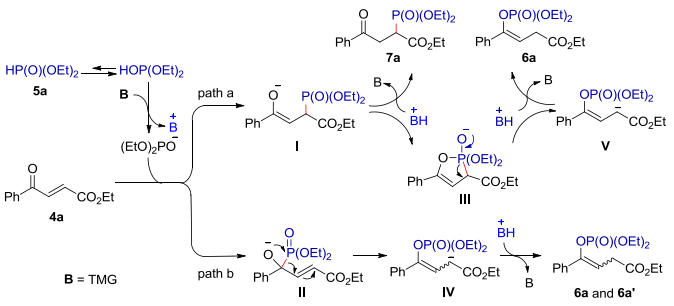


Fig. 2. X-ray crystal structure of enol phosphate **6o**.

Though further detailed mechanistic studies are needed, we proposed two possible pathways for this reaction based on the previous related work on phosphate chemistry (Scheme 2).[11] Taking the model reaction as example, in path **a**, the nucleophilic addition of $(EtO)_2P(OH)$ **5a** to the β-carbon of **4a** in the presence of base gave the enolate anion **I**. Then, the enolate anion **I** underwent the protonation to give the formal Michael adduct **7a** or cylization/rearrangement sequence to afford the corresponding product **6a**. However, we can't exclude the pathway **b** at the current stage, which involves the 1,2-addition of phosphite anion to the carbonyl group of **4a** and the subsequent phospha-Brook rearrangement to give the intermediate enol phosphate anion **IV**. The following protonation of enol phosphate anion **IV** should result in a *cis*/*trans* mixture of enol phosphate **6**. To get some insights into the possible mechanism, we carried out the reaction with **7a** under the optimal conditions in the presence of TMG and didn't observe any formation of **6a**. Moreover, the ^1H NMR analysis of the reaction mixture showed that only *cis*-configured products were observed. Therefore, path **a** (intramolecular cylization/rearrangement sequence) is more favorable than path **b**.



Scheme 2. Two possible pathways for the addition of phosphate **5a** to 4-oxo-enoate **4a**.

3. Conclusion

In summary, we have developed an efficient addition reaction of diethyl or diphenyl phosphite to 4-oxo-enoates by the use of simple and cheap TMG as the catalyst. The reaction provided a practical access to a wide range of enol phosphates. Considering the readily availability of the phosphorylation reagent and the operational simplicity of the procedure, the current methodology should find wide application in organic synthesis and medicinal chemistry. Further mechanistic study and synthetic transformations of the enol phosphates are still ongoing in our laboratory.

4. Experimental section

4.1. General information

Unless otherwise noted, materials were used as commercial suppliers. All solvents were purified by standard method. Flash column chromatography was performed using 200–300 mesh silica gel.

^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on Varian-Mercury 400/600 (400/600 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) in Hertz. Data are reported as follows: chemical shift (δ), multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, dd=doublet of doublets, m=multiplet). Mass spectra were measured on a Finnigan Trace MS spectrometer (EI) or API 2000 LC/MS/MS (ESI-MS). Elementary analyses were taken on a Vario EL III elementary analysis instrument.

4.2. 4-Oxo-enoates were prepared according to the literature procedures[7a]

*4.2.1. (E)-Ethyl 4-(3-chlorophenyl)-4-oxobut-2-enoate (**4k**).* Yellow solid, yield: 92%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (t, J=1.8 Hz, 1H), 7.84–7.89 (m, 2H), 7.59 (dd, J=8.0, 1.0 Hz, 1H), 7.47 (t, J=7.9 Hz, 1H), 6.90 (d, J=15.5 Hz, 1H), 4.31 (q, J=7.1 Hz, 2H), 1.36 (t, J=7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.1, 165.2, 138.0, 135.8, 135.3, 133.7, 133.2, 130.1, 128.7, 126.8, 61.5, 14.1 ppm. MS (EI) m/z 240 $(M+H)^+$.

*4.2.2. (E)-Ethyl 2-methyl-4-oxo-4-phenylbut-2-enoate (**4q**).* Colorless oil, 48% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96–7.98 (m, 2H), 7.72–7.73 (m, 1H), 7.60 (t, J=7.4 Hz, 1H), 7.50 (t, J=7.6 Hz, 2H), 4.31 (dd, J=14.3, 7.1 Hz, 2H), 2.19 (s, 3H), 1.37 (t, J=7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 167.3, 140.7, 137.4, 133.5, 131.7, 128.6, 61.5, 14.7, 14.1 ppm. MS (EI) m/z 218 (M^+).

4.3. General procedure for the synthesis of compounds 6a–6m

To a solution of 4-oxo-enoate **4** (0.2 mmol) and diethyl phosphite **5a** (0.4 mmol) in chloroform (1 mL) was added TMG (0.1 mmol) at room temperature. After completed (monitored by TLC analysis), the mixture was purified by column chromatography on silica gel (PE/EA=20/1∼5/1 as eluent) to afford the corresponding product **6**.

*4.3.1. (Z)-Ethyl 4-((diethoxyphosphoryl)oxy)-4-phenylbut-3-enoate (**6a**).* Colorless oil, 66% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J=7.9, 1.6 Hz, 2H), 7.31–7.37 (m, 3H), 5.85–5.89 (m, 1H), 4.01–4.21 (m, 6H), 3.47 (dd, J=7.0, 2.8 Hz, 2H), 1.21–1.30 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 147.5 (d, J=9.2 Hz), 134.9, 128.6, 128.2, 125.6, 109.3 (d, J=6.5 Hz), 64.4 (d, J=5.9 Hz), 60.7, 31.8, 15.9 (d, J=6.9 Hz), 14.1 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.27 ppm. FTIR (KBr, cm^{-1}): 3489, 3064, 2985, 2936, 2910, 1736, 1667, 1447, 1393, 1371, 1342, 1264, 1165, 1099, 1023, 983, 965, 887, 804, 768, 697, 625, 505. HRMS (ESI): Calcd for $C_{16}H_{23}O_6P$ $[M+Na]^+$: 365.1130; found: 365.1137.

*4.3.2. Ethyl 2-((diethoxyphosphoryl)oxy)-4-oxo-4-phenylbutanoate (**7a**).* Colorless oil, 24% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J=7.4 Hz, 2H), 7.59 (t, J=7.3 Hz, 1H), 7.47 (t, J=7.6 Hz, 2H), 4.16–4.25 (m, 6H), 3.80–3.88 (m, 1H), 3.63–3.73 (m, 1H), 3.41–3.49 (m, 1H), 1.26–1.39 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4 (d, J=15.3 Hz), 168.4, 136.0, 133.5, 128.6, 128.1, 62.91 (d, J=6.5 Hz), 128.2, 125.6, 109.3 (d, J=6.5 Hz), 61.6, 40.9, 39.5, 36.0, 16.3, 14.0 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 19.61 ppm. FTIR (KBr, cm^{-1}): 3470, 3063, 2983, 2933, 2873, 1734, 1690, 1598, 1581, 1449, 1392, 1369, 1259, 1222, 1158, 1097, 1024, 974, 891, 859, 800, 758, 692, 562, 511. HRMS (ESI): Calcd for $C_{16}H_{23}O_6P$ $[M+Na]^+$: 365.1130; found: 365.1104.

*4.3.3. (Z)-Methyl 4-((diethoxyphosphoryl)oxy)-4-phenylbut-3-enoate (**6b**).* Colorless oil, 57% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, J=8.0, 1.3 Hz, 2H), 7.32–7.37 (m, 3H), 5.85–5.89 (m, 1H), 4.01–4.15 (m, 4H), 3.72 (s, 3H), 3.49 (dd, J=6.9, 2.8 Hz, 2H), 1.21–1.25 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 147.5 (d, J=9.1 Hz), 134.8, 128.7, 128.2, 125.5, 109.1 (d, J=6.4 Hz), 64.5 (d, J=5.5 Hz), 51.9, 31.6, 15.9 (d, J=6.9 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.74 ppm. FTIR (KBr, cm^{-1}): 3484, 3063, 2987, 2911, 1739, 1667, 1494, 1443, 1395, 1351, 1262, 1207, 1164, 1100, 1021, 918, 887, 816, 768, 697, 624, 519. HRMS (ESI): Calcd for $C_{15}H_{21}O_6P$ $[M+Na]^+$: 351.0973; found: 351.1023.

*4.3.4. (Z)-Isopropyl 4-((diethoxyphosphoryl)oxy)-4-phenylbut-3-enoate (**6c**).* Colorless oil, 52% yield. ^1H NMR (400 MHz, $CDCl_3$)

δ 7.55 (dd, *J*=8.0, 1.5 Hz, 2H), 7.28–7.33 (m, 3H), 5.85–5.89 (m, 1H), 5.02–5.08 (m, 1H), 3.99–4.11 (m, 4H), 3.44 (dd, *J*=6.9, 2.9 Hz, 2H), 1.21–1.27 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 147.4 (d, *J*=9.0 Hz), 134.9, 128.6, 128.2, 125.6, 109.5 (d, *J*=6.2 Hz), 68.2, 64.4 (d, *J*=5.8 Hz), 32.1, 21.8, 15.9 (d, *J*=7.0 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.68 ppm. FTIR (KBr, cm^{-1}): 3386, 2983, 2937, 1732, 1667, 1494, 1448, 1371, 1266, 1179, 1107, 1018, 971, 908, 882, 819, 768, 698, 626, 504. HRMS (ESI): Calcd for $C_{17}H_{25}O_6P$ $[M+H]^+$: 357.1467; found: 357.1449.

*4.3.5. (Z)-Benzyl 4-((diethoxyphosphoryl)oxy)-4-phenylbut-3-enoate (**6d**).* Colorless oil, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J*=7.9, 1.6 Hz, 2H), 7.26–7.38 (m, 8H), 5.86–5.90 (m, 1H), 5.17 (s, 2H), 3.98–4.08 (m, 4H), 3.53 (dd, *J*=6.9, 2.8 Hz, 2H), 1.18–1.22 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 147.7 (d, *J*=8.9 Hz), 135.71, 134.9, 128.7, 128.5, 128.2, 125.6, 109.0 (d, *J*=6.3 Hz), 66.6, 64.5 (d, *J*=5.9 Hz), 31.8, 15.9 (d, *J*=6.9 Hz) ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.58 ppm. FTIR (KBr, cm^{-1}): 3477, 3064, 3034, 2985, 2937, 2910, 1960, 1886, 1736, 1687, 1601, 1496, 1449, 1389, 1345, 1261, 1159, 1100, 1023, 907, 817, 767, 698, 625, 506. HRMS (ESI): Calcd for $C_{21}H_{25}O_6P$ $[M+Na]^+$: 427.1286; found: 427.1263.

*4.3.6. (Z)-Ethyl 4-((diethoxyphosphoryl)oxy)-4-(p-tolyl)but-3-enoate (**6e**).* Colorless oil, 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J*=8.1 Hz, 2H), 7.15 (d, *J*=8.0 Hz, 2H), 5.80–5.84 (m, 1H), 3.99–4.20 (m, 6H), 3.45 (dd, *J*=6.9, 2.7 Hz, 2H), 2.35 (s, 3H), 1.23–1.30 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 147.6 (d, *J*=9.1 Hz), 138.6, 132.1, 128.9, 125.5, 108.3 (d, *J*=4.6 Hz), 64.4 (d, *J*=5.8 Hz), 60.7, 31.8, 21.2, 16.0 (d, *J*=6.9 Hz), 14.2 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.75 ppm. FTIR (KBr, cm^{-1}): 3490, 2984, 2933, 2873, 1737, 1667, 1613, 1513, 1447, 1394, 1371, 1342, 1265, 1166, 1099, 1030, 965, 889, 819, 761, 695, 632, 520. HRMS (ESI): Calcd for $C_{17}H_{25}O_6P$ $[M+H]^+$: 357.1467; found: 357.1445.

*4.3.7. (Z)-Ethyl 4-((diethoxyphosphoryl)oxy)-4-(4-fluorophenyl)but-3-enoate (**6f**).* Colorless oil, 62% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (dd, *J*=8.7, 5.3 Hz, 2H), 7.04 (t, *J*=8.6 Hz, 2H), 5.80–5.82 (m, 1H), 4.04–4.20 (m, 6H), 3.45 (dd, *J*=6.9, 2.7 Hz, 2H), 1.24–1.30 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 164.1, 161.6, 146.5 (d, *J*=8.8 Hz), 131.1, 127.5 (d, *J*=8.3 Hz), 115.2 (d, *J*=21.8 Hz), 109.2 (d, *J*=5.8 Hz), 64.5 (d, *J*=5.6 Hz), 60.9, 31.8, 16.0 (d, *J*=6.9 Hz), 14.2 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.57 ppm. FTIR (KBr, cm^{-1}): 3489, 3071, 2985, 2935, 2911, 1736, 1688, 1669, 1603, 1510, 1478, 1446, 1394, 1371, 1343, 1263, 1233, 1162, 1099, 1027, 984, 965, 890, 810, 520. HRMS (ESI): Calcd for $C_{16}H_{22}FO_6P$ $[M+Na]^+$: 383.1036; found: 383.1032.

*4.3.8. (Z)-Ethyl 4-(4-chlorophenyl)-4-((diethoxyphosphoryl)oxy)but-3-enoate (**6g**).* Colorless oil, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J*=8.6 Hz, 2H), 7.32 (d, *J*=8.6 Hz, 2H), 5.86–5.90 (m, 1H), 4.04–4.21 (m, 6H), 3.46 (dd, *J*=6.9, 2.8 Hz, 2H), 1.24–1.30 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 146.4 (d, *J*=9.0 Hz), 134.5, 133.4, 128.4, 126.9, 109.9 (d, *J*=6.2 Hz), 64.6 (d, *J*=5.8 Hz), 60.9, 31.8, 16.0 (d, *J*=6.8 Hz), 14.2 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.58 ppm. FTIR (KBr, cm^{-1}): 1635, 1619, 1591, 1562, 1530, 1497, 1472, 1447, 1410, 1391, 1320, 1300, 1245, 1146, 1097, 1048, 1030, 997, 908, 843, 797, 742, 729, 714, 684, 648, 625, 572, 523, 489. FTIR (KBr, cm^{-1}): 3486, 3069, 2984, 2936, 2910, 1736, 1689, 1593, 1491, 1446, 1399, 1370, 1342, 1263, 1165, 1094, 1026, 887, 819, 681, 629, 524. HRMS (ESI): Calcd for $C_{16}H_{22}ClO_6P$ $[M+Na]^+$: 399.0740; found: 399.0702.

*4.3.9. (Z)-Ethyl 4-(4-bromophenyl)-4-((diethoxyphosphoryl)oxy)but-3-enoate (**6h**).* Colorless oil, 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J*=8.6 Hz, 2H), 7.43 (d, *J*=8.7 Hz, 2H), 5.87–5.91 (m, 1H), 4.04–4.21 (m, 6H), 3.45 (dd, *J*=6.9, 2.8 Hz, 2H), 1.25–1.30 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 146.5 (d, *J*=9.0 Hz), 133.8, 131.4, 127.1, 122.8, 110.0 (d, *J*=6.5 Hz), 64.6 (d, *J*=5.7 Hz), 60.9, 31.8, 16.0 (d, *J*=6.8 Hz), 14.2 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.68 ppm. FTIR (KBr, cm^{-1}): 3489, 3069, 2984, 2936, 2909, 1909, 1734, 1689, 1587, 1487, 1446, 1396, 1370, 1342, 1261, 1162, 1099, 1071, 1024, 887, 818, 669, 627, 508. HRMS (ESI): Calcd for $C_{16}H_{22}BrO_6P$ $[M+H]^+$: 421.0416; found: 421.0369.

*4.3.10. (Z)-Ethyl 4-((diethoxyphosphoryl)oxy)-4-(4-methoxyphenyl) but-3-enoate (**6i**).* Colorless oil, 38% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J*=8.8 Hz, 2H), 6.87 (d, *J*=8.8 Hz, 2H), 5.72–5.76 (m, 1H), 4.02–4.20 (m, 6H), 3.82 (s, 3H), 3.44 (dd, *J*=6.9, 2.8 Hz, 2H), 1.23–1.30 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 159.9, 147.3 (d, *J*=9.1 Hz), 127.5, 127.0, 113.5, 107.4 (d, *J*=6.5 Hz), 64.5 (d, *J*=5.8 Hz), 60.7, 55.2, 31.8, 16.0 (d, *J*=7.0 Hz), 14.2 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.76 ppm. FTIR (KBr, cm^{-1}): 3474, 2984, 2934, 2843, 1736, 1667, 1609, 1513, 1463, 1446, 1392, 1371, 1258, 1174, 1099, 1027, 889, 801, 761, 626, 504. HRMS (ESI): Calcd for $C_{17}H_{25}O_7P$ $[M+Na]^+$: 395.1236; found: 395.1221.

*4.3.11. Ethyl 2-(diethoxyphosphoryl)-4-(4-methoxyphenyl)-4-oxobutanoate (**7i**).* Colorless oil, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J*=8.5 Hz, 2H), 6.94 (d, *J*=8.4 Hz, 2H), 4.17–4.25 (m, 6H), 3.87 (s, 3H), 3.62–3.80 (m, 2H), 3.37–3.43 (m, 1H), 1.28–1.39 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8 (d, *J*=15.5 Hz), 168.5 (d, *J*=5.0 Hz), 163.7, 130.4, 129.0, 113.7, 62.9 (d, *J*=5.1 Hz), 61.6, 55.4, 40.9, 39.5, 35.5, 16.3, 14.0 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ 19.84 ppm. FTIR (KBr, cm^{-1}): 3470, 2968, 2843, 2770, 2577, 2410, 2049, 1736, 1677, 1601, 1512, 1463, 1366, 1260, 1157, 1097, 1023, 894, 834, 802, 765, 712, 636, 608, 563, 505, 434. MS (EI) *m/z* 375 $(M+H)^+$.

*4.3.12. (Z)-Ethyl 4-((diethoxyphosphoryl)oxy)-4-(3-methoxyphenyl) but-3-enoate (**6j**).* Colorless oil, 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.30 (m, 1H), 7.15 (d, *J*=7.8 Hz, 1H), 7.09 (t, *J*=1.8 Hz, 1H), 6.87 (dd, *J*=8.1, 2.5 Hz, 1H), 5.87–5.91 (m, 1H), 4.04–4.21 (m, 6H), 3.82 (s, 3H), 3.47 (dd, *J*=6.9, 2.8 Hz, 2H), 1.23–1.30 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 159.3, 147.2 (d, *J*=9.1 Hz), 136.2, 129.2, 118.0, 114.4, 110.9, 109.5 (d, *J*=6.4 Hz), 64.4 (d, *J*=5.8 Hz), 60.7, 55.2, 31.8, 15.9 (d, *J*=7.0 Hz), 14.1 ppm ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.73 ppm. FTIR (KBr, cm^{-1}): 3489, 3070, 2984, 2839, 1943, 1908, 1868, 1735, 1668, 1602, 1583, 1489, 1432, 1394, 1371, 1263, 1209, 1164, 1098, 1024, 974, 916, 798, 700, 664, 637, 506, 485. HRMS (ESI): Calcd for $C_{17}H_{25}O_7P$ $[M+Na]^+$: 395.1236; found: 395.1166.

*4.3.13. (Z)-Ethyl 4-(3-chlorophenyl)-4-((diethoxyphosphoryl)oxy) but-3-enoate (**6k**).* Colorless oil, 53% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.44–7.45 (m, 1H), 7.28–7.29 (m, 2H), 5.89–5.92 (m, 1H), 4.06–4.20 (m, 6H), 3.46 (dd, *J*=6.8, 2.6 Hz, 2H), 1.25–1.30 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 146.1 (d, *J*=9.0 Hz), 136.7, 134.2, 129.5, 128.6, 125.6, 123.7, 110.6 (d, *J*=6.2 Hz), 64.5 (d, *J*=5.7 Hz), 60.8, 31.8, 15.9 (d, *J*=6.8 Hz), 14.1 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.71 ppm. FTIR (KBr, cm^{-1}): 3491, 3069, 2984, 2936, 2910, 1736, 1693, 1667, 1595, 1568, 1477, 1445, 1418, 1394, 1371, 1342, 1263, 1166, 1098, 1027, 968, 903, 790, 745, 696, 633, 532, 470. HRMS (ESI): Calcd for $C_{16}H_{22}ClO_6P$ $[M+H]^+$: 377.0921; found: 377.0868.

*4.3.14. (Z)-Ethyl 4-(3-bromophenyl)-4-((diethoxyphosphoryl)oxy) but-3-enoate (**6l**).* Colorless oil, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.47 (dd, *J*=16.8, 8.0 Hz, 2H), 7.22 (t, *J*=7.9 Hz, 1H), 5.88–5.92 (m, 1H), 4.07–4.21 (m, 6H), 3.46 (dd, *J*=6.9, 2.8 Hz, 2H), 1.25–1.31 (m, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 146.0 (d, *J*=8.9 Hz), 136.9, 131.5, 129.7, 128.5, 124.1, 122.3, 110.6 (d, *J*=5.8 Hz), 64.5 (d, *J*=5.6 Hz), 60.8, 31.8, 15.9 (d, *J*=6.9 Hz),

14.1 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −6.74 ppm. FTIR (KBr, cm^{-1}): 3487, 3067, 2983, 2935, 2909, 1736, 1691, 1593, 1563, 1475, 1445, 1414, 1394, 1370, 1261, 1213, 1161, 1098, 1024, 967, 898, 859, 799, 748, 694, 631, 528, 504, 465. HRMS (ESI): Calcd for $C_{16}H_{22}BrO_6P$ $[M+Na]^+$: 443.0235; found: 443.0232.

*4.3.15. (Z)-Ethyl 4-((diethoxyphosphoryl)oxy)-4-(2-methoxyphenyl) but-3-enoate (**6m**).* Colorless oil, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, J=7.6, 1.7 Hz, 1H), 7.28–7.33 (m, 1H), 6.89–6.96 (m, 2H), 5.79–5.83 (m, 1H), 4.17 (q, J=7.1 Hz, 2H), 3.93–4.08 (m, 4H), 3.85 (s, 3H), 3.46 (dd, J=6.9, 2.6 Hz, 2H), 1.28 (t, J=7.1 Hz, 3H), 1.17–1.21 (m, 6H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.3, 156.9, 144.6 (d, J=8.9 Hz), 130.0, 124.1, 120.1, 112.4 (d, J=7.2 Hz), 110.8, 64.1 (d, J=6.3 Hz), 60.6, 55.4, 31.7, 15.8 (d, J=7.0 Hz, 7H), 14.1 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −7.18 ppm. FTIR (KBr, cm^{-1}): 3485, 2984, 2842, 1739, 1676, 1606, 1577, 1513, 1446, 1416, 1368, 1258, 1162, 1101, 1025, 980, 892, 836, 802, 758, 639, 588, 528. HRMS (ESI): Calcd for $C_{17}H_{25}O_7P$ $[M+Na]^+$: 395.1236; found: 395.1205.

4.4. General procedure for the synthesis of compounds 6n–6r

To a solution of 4-oxo-enoate **4** (0.2 mmol) and diphenyl phosphite **5b** (0.4 mmol) in toluene (2 mL) was added TMG (0.1 mmol) at −20 °C. After completed (monitored by TLC analysis), the mixture was purified by column chromatography on silica gel (PE/EA=20/1–10/1 as eluent) to afford the corresponding product **6**.

*4.4.1. (Z)-Ethyl 4-((diphenoxyphosphoryl)oxy)-4-phenylbut-3-enoate (**6n**).* Colorless oil, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.53 (m, 2H), 7.28–7.30 (m, 7H), 7.10–7.17 (m, 6H), 5.93–5.97 (m, 1H), 4.11 (q, J=7.1 Hz, 2H), 3.40 (dd, J=7.0, 2.9 Hz, 2H), 1.22 (t, J=7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 150.2 (d, J=7.3 Hz), 147.5 (d, J=9.5 Hz), 134.0, 129.6, 128.8, 125.5 (d, J=15.7 Hz), 119.9 (d, J=4.8 Hz), 109.9 (d, J=6.9 Hz), 60.7, 31.6, 14.0 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −18.23 ppm. FTIR (KBr, cm^{-1}): 3453, 3066, 2982, 2936, 2906, 2378, 1948, 1887, 1734, 1670, 1592, 1490, 1449, 1371, 1261, 1215, 1160, 1022, 960, 906, 765, 690, 619, 578, 517. HRMS (ESI): Calcd for $C_{24}H_{23}O_6P$ $[M+Na]^+$: 461.1130; found: 461.1066.

*4.4.2. (Z)-Methyl 4-(4-bromophenyl)-4-((diphenoxyphosphoryl)oxy) but-3-enoate (**6o**).* Colorless oil, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J=8.6 Hz, 2H), 7.35 (d, J=8.6 Hz, 2H), 7.31 (t, J=7.9 Hz, 4H), 7.19 (t, J=7.4 Hz, 2H), 7.12 (d, J=7.8 Hz, 4H), 5.92–5.94 (m, 1H), 3.66 (s, 3H), 3.39 (dd, J=7.0, 2.8 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 150.2 (d, J=7.2 Hz), 146.7 (d, J=9.3 Hz), 133.1, 131.5, 129.8, 127.2, 125.6, 123.1, 119.9 (d, J=4.8 Hz), 110.43 (d, J=6.8 Hz), 52.0, 31.4 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −18.44 ppm. FTIR (KBr, cm^{-1}): 3370, 3070, 2953, 2836, 1738, 1689, 1671, 1591, 1591, 1489, 1456, 1438, 1397, 1260, 1213, 1160, 1098, 1073, 1026, 951, 818, 759, 689, 621, 503. MS (EI) m/z 503 $(M+H)^+$. EA: Calcd for $C_{23}H_{20}BrO_6P$: C, 54.89; H, 4.01; found: C, 54.79; H, 4.19.

*4.4.3. (Z)-Ethyl 4-((diphenoxyphosphoryl)oxy)-4-(4-nitrophenyl) but-3-enoate (**6p**).* Colorless oil, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J=8.8 Hz, 2H), 7.63 (d, J=8.8 Hz, 2H), 7.33 (t, J=7.8 Hz, 4H), 7.21 (m, 3H), 7.15 (d, J=7.7 Hz, 3H), 6.16–6.20 (m, 1H), 4.16 (m, 2H), 3.45 (dd, J=6.9, 2.9 Hz, 2H), 1.25 (t, J=7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 150.1 (d, J=7.3 Hz), 147.7, 145.6 (d, J=9.0 Hz), 140.2, 129.9, 126.2, 125.8, 123.6, 119.9 (d, J=4.9 Hz), 114.2 (d, J=6.5 Hz), 61.1, 31.8, 14.1 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −18.18 ppm. FTIR (KBr, cm^{-1}): 3454, 3073, 2984, 2939, 2907, 2453, 1944, 1872, 1736, 1666, 1595, 1521, 1489, 1346, 1261, 1213, 1161, 1100, 1025, 963, 853, 811, 756, 691, 621, 576, 507. HRMS (ESI): Calcd for $C_{24}H_{22}NO_8P$ $[M+H]^+$: 484.1161; found: 484.1066.

*4.4.4. (Z)-Ethyl 4-((diphenoxyphosphoryl)oxy)-4-(3-nitrophenyl)but-3-enoate (**6q**).* Colorless oil, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (t, J=1.8 Hz, 1H), 8.14 (dd, J=8.1, 2.0 Hz, 1H), 7.81 (d, J=7.9 Hz, 1H), 7.46 (d, J=8.0 Hz, 1H), 7.32 (t, J=7.9 Hz, 4H), 7.15–7.21 (m, 6H), 6.09–6.13 (m, 1H), 4.15 (q, J=7.1 Hz, 2H), 3.44 (dd, J=6.9, 2.9 Hz, 2H), 1.26 (d, J=7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 150.1 (d, J=7.1 Hz), 148.2, 145.3 (d, J=9.0 Hz), 136.0, 131.3, 129.9, 129.4, 125.7, 123.5, 120.6 119.8 (d, J=4.7 Hz), 112.9 (d, J=6.5 Hz), 61.1, 31.7, 14.1 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −18.23 ppm. FTIR (KBr, cm^{-1}): 3384, 3077, 2984, 1946, 1733, 1591, 1533, 1489, 1350, 1260, 1212, 1160, 1099, 1026, 964, 853, 807, 769, 688, 619, 582, 503. HRMS (ESI): Calcd for $C_{24}H_{22}NO_8P$ $[M+Na]^+$: 506.0981; found: 506.0962.

*4.4.5. (Z)-Ethyl 4-((diphenoxyphosphoryl)oxy)-2-methyl-4-phenylbut-3-enoate (**6r**).* Colorless oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.53 (m, 2H), 7.28–7.33 (m, 6H), 7.14–7.20 (m, 5H), 7.06 (d, J=8.4 Hz, 2H), 5.78 (dd, J=10.0, 1.7 Hz, 1H), 4.06–4.15 (m, 2H), 3.74–3.82 (m, 1H), 1.31 (d, J=7.1 Hz, 3H), 1.21 (t, J=7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 150.4, 146.6 (d, J=9.5 Hz), 134.4, 129.7 (d, J=5.0 Hz), 128.9, 128.3, 125.9, 125.4 (d, J=12.0 Hz), 120.0 (dd, J=16.6, 4.8 Hz), 116.8 (d, J=6.9 Hz), 60.8, 37.3, 18.1, 14.1 ppm; ^{31}P NMR (161 MHz, $CDCl_3$) δ −18.4 ppm. FTIR (KBr, cm^{-1}): 3386, 2983, 2449, 1732, 1662, 1632, 1596, 1491, 1374, 1259, 1215, 1187, 1161, 1095, 1023, 966, 811, 756, 692, 521. HRMS (ESI): Calcd for $C_{25}H_{25}O_6P$: $[M+Na]^+$: 475.1286; found: 475.1287.

Acknowledgements

We are grateful to the National Science Foundation of China (NO. 21072069 and 21002036), the National Basic Research Program of China (2011CB808603), and the Program for Chang-jiang Scholars and Innovation Research Team in University (IRT0953) for support of this research.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2012.05.021.

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