Tetrahedron 72 (2016) 3084–3091

Contents lists available at ScienceDirect

Tetrahedron

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

Silver-catalyzed direct regioselective phosphonation of β-aryl-α,β-unsaturated carbonyl compounds with *H*-phosphites under microwave irradiation

Jin-Wei Yuan [a,*], Yuan-Zhe Li [a], Wen-Peng Mai [b], Liang-Ru Yang [a], Ling-Bo Qu [a,*]

[a] School of Chemistry & Chemical Engineering, Henan University of Technology, Academician Workstation for Natural Medicinal Chemistry of Henan Province, Zhengzhou 450001, PR China
[b] School of Materials and Chemical Engineering, Henan Institute of Engineering, Zhengzhou 451191, PR China

ARTICLE INFO

Article history:
Received 28 February 2016
Received in revised form 10 April 2016
Accepted 12 April 2016
Available online 13 April 2016

Keywords:
Silver-catalyzed
β-Aryl-α,β-unsaturated carbonyl compound
Alkenylphosphonate
Radical reaction
Phosphonation

ABSTRACT

An efficient protocol for silver-catalyzed direct radical phosphonation of β-aryl-α,β-unsaturated carbonyl compounds with *H*-phosphites to afford *trans*-substituted alkenylphosphonates under microwave irradiation is described. Some notable features of this method are high efficiency, good yield, broad functional groups tolerance, commercially available and cheap catalyst.

1. Introduction

Alkenylphosphonates are especially useful small organic molecules.[1] In addition to their extensive use in polymer science as copolymers, they are routinely used as building blocks for the introduction of remote phosphonate functional groups or to prepare biologically active molecules.[2] Quite recently, the alkenylphosponate scaffold itself has been used as a promising pharmacophore. They have also been shown over the years to be key starting materials for an impressive range of chemical transformations.[3] Not surprisingly, numerous reports on the synthesis of alkenylphosphonates have appeared in the presence of $Mn(OAc)_3$ during the past decade.[4] Moreover, the synthesis of arylalkene phosphonates have also been reported. A stereoselective procedure for the preparation of alkenylphosphonates by copper-mediated cross-coupling between 1,1-dibromo-1-alkenes and dialkyl phosphites was reported by Evano and co-workers group, and $Mn(OAc)_3$-mediated tandem phosphonyl radical addition to β-nitrostyrenes followed by denitration to produce 2-alkenyl phosphonates was described by Pan's group.[5] Wu group reported a silver-catalyzed synthesis of 3-phosphorated coumarins via radical cyclization of alkynonates and dialkyl phosphites.[6] However, similar reactions of the corresponding β-aryl-α,β-unsaturated carbonyl compounds with *H*-phosphites have remained underexplored.

The same reaction was once employed by the coupling of β-aryl-α,β-unsaturated carbonyl compounds with *H*-phosphites. There maybe be two challenges: (1) how to control the reaction position of α,β-unsaturated carbonyl compounds, and (2) how to control the regio- and stereochemistry of the newly formed alkenylphosphonates. A significant amount of efforts have been spent on the coupling reaction of α,β-unsaturated carbonyl compounds with *H*-phosphites. However, the literature search indicated that only few examples described the reaction of β-aryl-α,β-unsaturated carbonyl compounds and *H*-phosphites. Reetz's and Robinson's groups reported a synthetic procedure of triethyl benzylidene phosphonoacetate by Knoevenagel condensation reaction of triethyl phosphonoacetate with benzaldehyde (Scheme 1a).[7] Zou's group described an oxidant coupling reaction of β-aryl-α,β-unsaturated carbonyl compounds and *H*-phosphites in AcOH solvent using $Mn(OAc)_3$ as an oxidant (Scheme 1b).[8] Despite these methods having various levels of success, there still exist some problems, such as: requirement of complicated starting materials, a narrow

* Corresponding authors. E-mail addresses: yuanjinweigs@126.com (J.-W. Yuan), qulingbo@haut.edu.cn (L.-B. Qu).

http://dx.doi.org/10.1016/j.tet.2016.04.034
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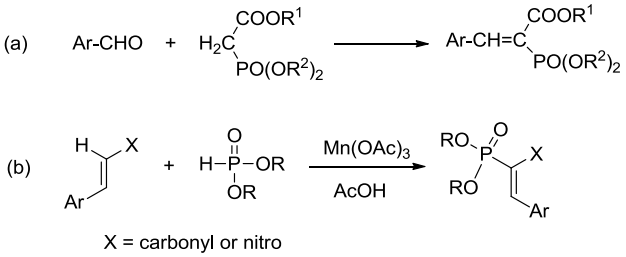
Previous works:



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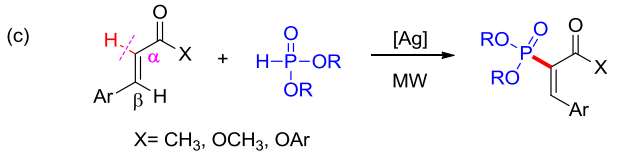


Scheme 1. Synthesis of phosphonates of β-aryl-α,β-unsaturated carbonyl compounds.

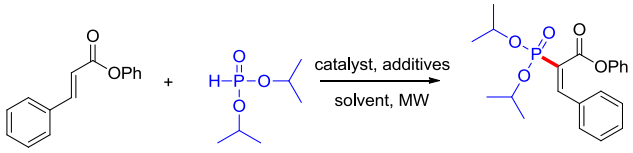
scope of substrates, high temperature, a toxic catalyst or an acid environment. Therefore, developing a general and applicable strategy for the synthesis of phosphonate derivatives of β-aryl-α,β-unsaturated carbonyl compounds is still desirable.

Transition metal-catalyzed dehydrogenative coupling reaction is a fundamental method for the construction of new chemical bonds. By employing this method, two substrates can be coupled without any prefunctionalization. The preparation of phosphonate derivatives via this dehydrocoupling method has recently attracted great attention using $Pd(OAc)_2/AgBF_4$, $Ni(OAc)_2$, $Pd(OAc)_2/Mn(OAc)_3$, $AgNO_3/K_2S_2O_8$, $AgNO_3$, or DTBP as the catalysts.[9] Microwave irradiation is used as an alternative thermal energy source to conventional heating in organic synthesis. The use of microwave irradiation has been applied to a wide range of reaction types. Many of these reactions have been demonstrated to result in higher yield and/or selectivity under microwave irradiation.[10] Herein, we disclose an efficient silver-catalyzed direct dehydrogenative coupling of β-aryl-α,β-unsaturated carbonyl compounds with *H*-phosphites to selectively produce the valuable *E*-isomer, alkenylphosphonates (α-phosphonato-α,β-unsaturated carbonyl compounds) in high yields under microwave irradiation, which opens a new route for the modification at α-phosphonation of β-aryl-α,β-unsaturated carbonyl compounds (Scheme 1c).

2. Results and discussion

Our previous study showed that the phosphonyl radicals could be easily generated from *H*-phosphites with a catalytic amount of silver salts, and the phosphonation of coumarins has been developed with this procedure.[9b] Based on this achievement, the model reaction of phenyl cinnamate (**1a**) and diisopropyl *H*-phosphite (**2a**) was carried out in the presence of $AgNO_3$ (10 mol%) without any the additive in CH_3CN at 90 °C under microwave irradiation for 20 min. Fortunately, the product was detected, and the isolated yield was 20% (Table 1, entry 1). Spectroscopic data were in agreement with the assigned structure of compound **3a**. High-resolution mass spectrometry shows a clear molecular ion peak at *m/z* 389.1514 $[M+H]^+$, which shows that only one proton atom was substituted. ^{31}P NMR indicated a single peak at δ=10.9 ppm. The α carbon atom at δ_C=133.8 ppm appears as a doublet with a coupling constant, $^1J_{P-C}$=19.5 Hz. The carbon atoms of carbonyl group and β position also appear as a doublet with a smaller

Table 1
Optimization of reaction conditions[a]



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

Entry	Catalyst (mol%)	Additive (equiv)	Solvent	Temp (°C)	Time (min)	Yield[b] (%)
1	$AgNO_3$ (10)	—	CH_3CN	90	20	20
2	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (1.0)	CH_3CN	90	20	70
3	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	CH_3CN	90	20	82
4	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.3)	CH_3CN	90	20	79
5	$AgNO_3$ (10)	$Cu(NO_3)_2$ (0.5)	CH_3CN	90	20	<5
6	$AgNO_3$ (10)	$NaNO_3$ (0.5)	CH_3CN	90	20	22
7	$AgNO_3$ (10)	HNO_3[c] (0.5)	CH_3CN	90	20	41
8	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	20	88
9	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	EtOAc	82	20	78
10	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	MeOH	90	20	<5
11	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	H_2O	90	20	nr[d]
12	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	Dioxane	90	20	75
13	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	DCE	90	20	70
14	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	30	20	25
15	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	40	20	52
16	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	50	20	63
17	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	60	20	72
18	Ag_2CO_3 (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	20	80
19	AgOTf (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	20	75
20[e]	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	20	45
21[f]	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	20	80
22	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	1	50
23	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	3	75
24	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	5	80
25	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	10	90
26[g]	$AgNO_3$ (10)	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	6 h	80
27	—	$Mg(NO_3)_2·6H_2O$ (0.5)	THF	70	10	nr

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), catalyst, and additive in solvent (2 mL) was stirred for 20 min under microwave irradiation. The given equivalents (equiv) and mol% are related to **1a**.
[b] Isolated yield.
[c] HNO_3 is 65% concentrated nitric acid.
[d] nr=no reaction.
[e] 1.0 equiv **2a** was used.
[f] 3.0 equiv **2a** was used.
[g] No microwave irradiation.

coupling constant, $^{2}J_{P-C}$=12.4 Hz and $^{2}J_{P-C}$=6.5 Hz, respectively. This fact demonstrated that the phosphonyl group was attached to α position as expected. The *E* or *Z* stereochemistry of **3a** is easily made by the ^{1}H NMR analysis of the coupling constant between the phosphorus atom and a hydrogen atom in β position. Indeed many reports in the literature have shown that the classical range of values is $^{3}J_{P-H}$=30–50 Hz when both phosphorus group and phenyl are in Z stereoisomer, and $^{3}J_{P-H}$=10–30 Hz when both groups are in *E* stereoisomer.[11] The β hydrogen atom of **3a** at δ_{H}=7.81 ppm appears as a doublet with a coupling constant, $^{3}J_{P-H}$=23.8 Hz, which proves that the stereochemistry of **3a** is an *E* stereoisomer.

To identify the optimal reaction conditions, the extensive screening experiments were carried out. When 1.0 equiv of $Mg(NO_3)_2\cdot 6H_2O$ was employed as an additive, the target product **3a** was isolated in 70% yield (Table 1, entry 2). Excitingly, the product yield of **3a** could reach 82% using 0.5 equiv of $Mg(NO_3)_2\cdot 6H_2O$ (Table 1, entries 3–4). The nitrate ion maybe be essential to the reaction efficiency. Several other nitrates and HNO_3 were tested, and 0.5 equiv of $Mg(NO_3)_2\cdot 6H_2O$ proved to be the best result (Table 1, entries 3, 5–7). Different magnesium salts, $MgCl_2$ (0.5 equiv) and $MgSO_4$ (0.5 equiv) were also examined, and their yields are 23% and 25%, respectively. These results showed that $Mg(NO_3)_2\cdot 6H_2O$ was the best choice as the adductive. Other solvents, such as THF, EtOAc, MeOH, H_2O, dioxane and DCE were applied instead of CH_3CN. THF was clearly the best choice for this reaction, and the yield of **3a** could reach 88% (Table 1, entries 8–13). Various reaction temperatures were investigated, and 70 °C was found to be the best choice (Table 1, entries 8, 14–17). Different the catalysts of silver salts were also evaluated, and proved to be less effective compared with $AgNO_3$ (Table 1, entries 18–19). In an attempt to further increase the yield of this reaction, the loading of **2a** was decreased or increased. Unfortunately, both led to the lower yields (Table 1, entries 20–21). Various reaction times were also examined, and 10 min was found to be best choice (Table 1, entries 22–25). In the absence of microwave irradiation, the yield of **3a** could reach 80% but required a longer reaction time for 6.0 h (Table 1, entry 26). Additionally, without the silver salt catalyst, $Mg(NO_3)_2\cdot 6H_2O$ alone could not promote this reaction (Table 1, entry 27).

With the optimized reaction conditions in hand (Table 1, entry 25), the scope and limitation of the dehydrogenation coupling reactions were explored with various α,β-unsaturated carbonyl compounds with *H*-phosphites (Table 2). Firstly, various phenyl cinnamate with *ortho*-, *meta*- and *para*-substituent on the aryl ring were evaluated. The reaction could proceed well using various substituted phenyl cinnamates and diisopropyl *H*-phosphite to form the corresponding products in moderate to good yields (**3a**–**3g**). Comparing with phenyl cinnamates associated with electron-donating (−CH_3, −OCH_3), the reaction of phenyl cinnamates substituted with electron-withdrawing groups (−F, −Cl, −NO_2) gave better results. The substrate containing a strong electron-withdrawing group (−NO_2) also proceeded smoothly, giving the target product in 85% yield (**3d**). Interestingly, methyl cinnamate and 4-phenylbut-3-en-2-one were used as the reaction substrates, the products (**3h** and **3i**) were obtained in 88% and 52% yields. Gratifyingly, all these dehydrogenation coupling reactions proceeded regioselectively. The phosphonyl group was attached to α-position of α,β-unsaturated carbonyl compounds as expected, and the *E* stereochemistry of **3** were easily made. Notably, a 63% yield of **3j** was produced by the reaction of β-nitrostyrene and diisopropyl *H*-phosphite, and the reaction was realized by the phosphonyl addition to β-nitrostyrene followed by the denitration to form the corresponding product. Unfortunately, 3-phenylacrylamide failed to deliver the desired products with the current reaction condition (**3k**).

Subsequently, the scope of various dialkyl *H*-phosphites was also investigated. The reaction could proceed smoothly using different dialkyl *H*-phosphites and phenyl cinnamate to form the corresponding products in moderate to good yields (**3l**–**3p**). The diisopropyl *H*-phosphite gave the best yield 90% (**3a**), and the di-*n*-propyl *H*-phosphite produced the lowest yield 60% (**3n**). Moreover, diphenylphosphine oxide was employed, and a 46% yield of **3q** could also be made. Using the standard reaction condition, the corresponding target products were produced in moderate to good yields (**3r**–**3w**).

To certify the mechanism of this transformation, a controlled experiment was performed (Scheme 2). The reaction of phenyl cinnamate (**1a**) with diisopropyl *H*-phosphite (**2a**) was carried out under the standard conditions by the addition of 3.0 equiv radical scavenger 2,2,6,6-tetramethylpiperidinooxy (TEMPO). The reaction was suppressed, and only trace of target product (**3a**) was detected. The result indicated that the reaction might proceed via a radical pathway.

Based on the above result and previous studies,[9b,12] a possible reaction mechanism was proposed as shown in Scheme 3. Firstly, diisopropyl *H*-phosphite (**2a**) reacts with $AgNO_3$ to produce the intermediate **A**, and then a phosphonyl radical **B** is generated from the intermediate **A**. The electrophilic diisopropyl phosphonyl radical **B** is more reactive toward conjugated alkene than the phenyl rings. Since α-position of the conjugated alkene maybe have a higher electron density than β-position, it induces the phosphonyl radical **B** attacking α-position to generate benzyl radical **C**. In order to prove this deduction, the competing reaction pathway was made by theoretical calculation (Scheme 4). As shown in Scheme 4, there are two possible reaction pathways associated with the attack by the phosphonyl radical **B** on the different carbon atom (α or β) of **1a**, and the energy barrier via TS1α (15.33 kcal/mol) is 1.17 kcal/mol lower than that via TS1β (16.50 kcal/mol), indicating the attack on the α-position carbon of **1a** by the phosphonyl radical **B** should be energetically favorable. The benzyl radical **C** is transformed into a more stable conformation **D**. Radical **D** is oxidized with Ag(I) to benzyl carbocation **E** followed by deprotonation to regenerate the conjugated system and afford the phosphonation product **3a** as an *E*-isomer.

3. Conclusion

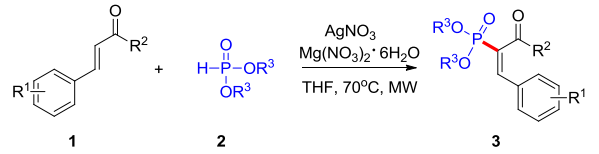
In conclusion, we have developed an efficient protocol for the synthesis of alkenylphosphonates via silver-catalyzed direct and regioselective phosphonation reaction of β-aryl-α,β-unsaturated carbonyl compounds. The dehydrogenation coupling reaction is straightforward and highly efficient, and various *trans*-substituted alkenylphosphonates were obtained in the mediate to good yields.

4. Experimental section

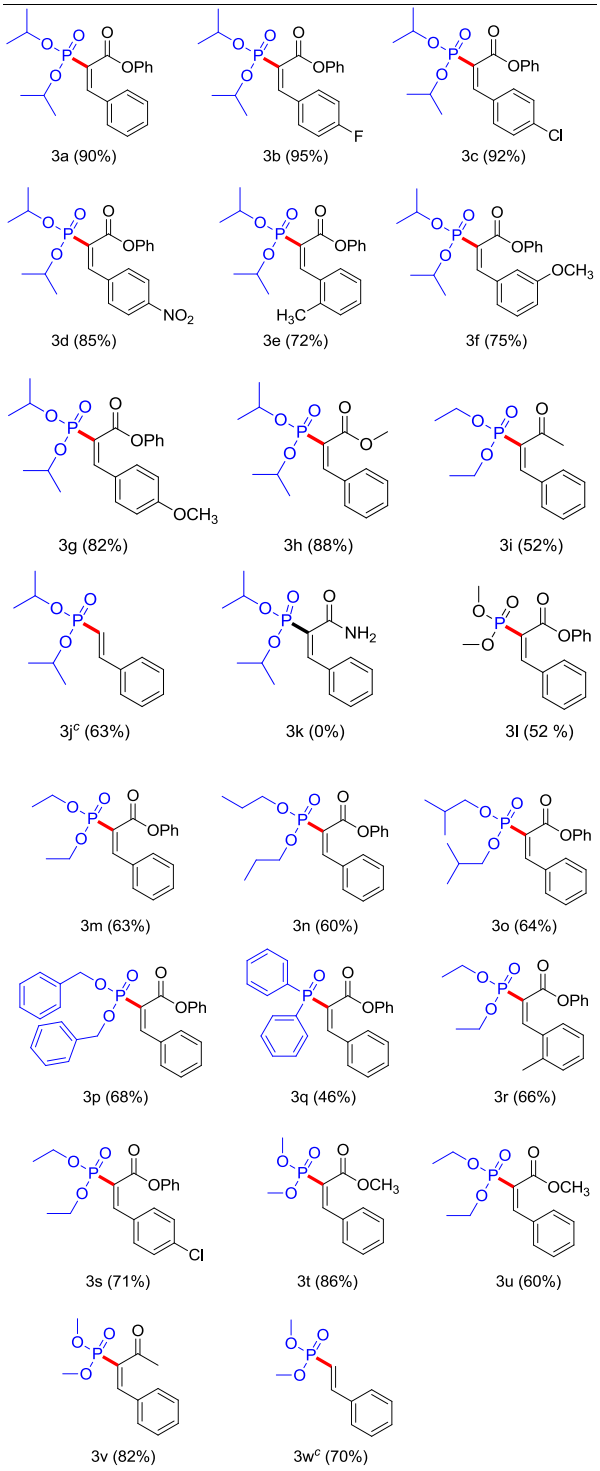
4.1. General information

All substrates were purchased from *J* & *K* Scientific Ltd. without further purification. Nuclear magnetic resonance spectra were recorded on Bruker Avance 400 MHz spectrometer. Chemical shifts for ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, m=multiplet and br=broad), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane. Chemical shift for ^{31}P NMR spectra are recorded relative to 85% H_3PO_4 (δ=0 ppm) as external standard. High resolution mass spectra (HRMS) were obtained on Q-TOF instrument using the ESI technique. IR spectra were recorded on Shimadazu IR-408 fourier transform infrared spectrophotometer using a thin film

Table 2
Silver-catalyzed direct phosphonation of β-aryl-α,β-unsaturated carbonyl compounds with *H*-phosphites producing alkenylphosphonates **3**[a,b]



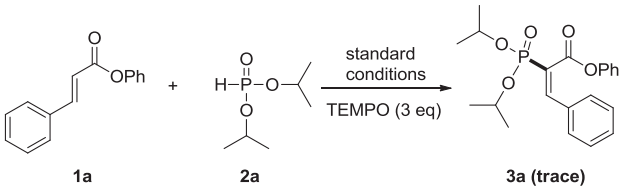
1 **2** **3**



[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), 10 mol% $AgNO_3$ catalyst, $Mg(NO_3)_2{\cdot}6H_2O$ additive (0.125 mmol), solvent (2 mL), 70 °C, 10 min under microwave irradiation.

[b] Isolated yield.

[c] **3j** and **3w** were produced using (*E*)-(2-nitrovinyl)benzene as the substrate.



Scheme 2. A controlled experiment.

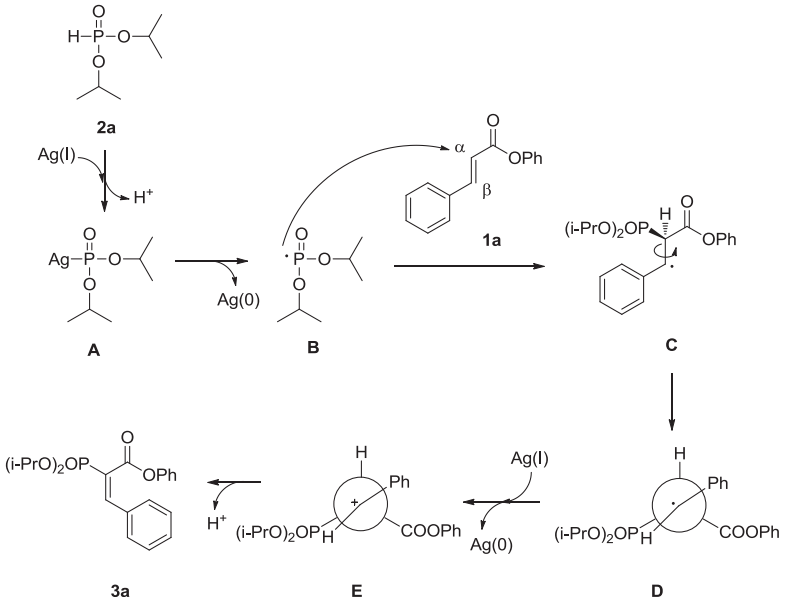
supported on KBr pellets. Melting points were measured on an XT4A microscopic apparatus and were uncorrected.

4.2. General experimental procedure for synthesis of products (3a–3w)

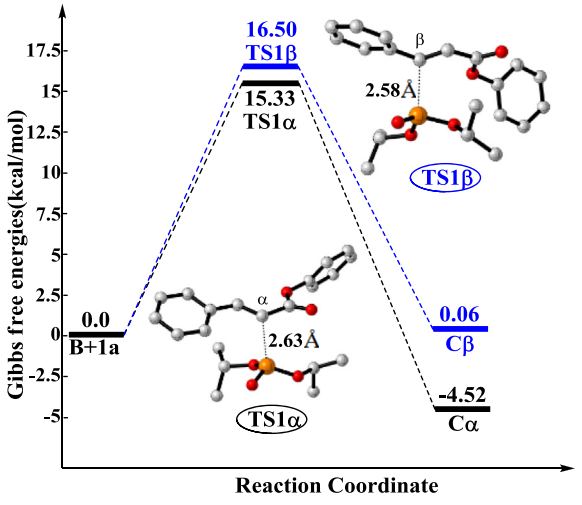
Arylalkenes **1** (0.25 mmol), dialkyl *H*-phosphite **2** (0.5 mmol), $AgNO_3$ (0.025 mmol, 4.2 mg) and $Mg(NO_3)_2{\cdot}6H_2O$ (0.25 mmol, 64 mg) in anhydrous THF (2 mL) were added to a 5 mL microwave reaction tube. The mixture was heated at 70 °C for 10 min under microwave irradiation. After completion of the reaction, the solvent was distilled under vacuum. 15 mL ethylacetate was added to the residuum, 20 mL 5% $NaHCO_3$ was added to wash two times, and 10 mL saturated NaCl solution washed one time. The organic phase was dried with anhydrous Na_2SO_4. The solvent was distilled under vacuum. The crude product was purified by silica gel column chromatography to give the desired product **3** using ethyl acetate/petroleum ether (1:5 to 2:1) as the eluant.

*4.2.1. (E)-Phenyl 2-(diisopropoxyphosphoryl)-3-phenylacrylate (**3a**).* 87.3 mg (yield 90%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2979, 2869 (−CH_3), 1743 (C═O), 1591, 1491 (Ar−), 1254 (P═O), 1173 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.81 (d, J_{P-H}=23.8 Hz, 1H), 7.56–7.53 (m, 2H), 7.44–7.36 (m, 5H), 7.23 (t, J_{H-H}=7.4 Hz, 1H), 7.05 (dd, J_{H-H}=8.7 Hz, J_{H-H}=1.1 Hz, 2H), 4.85–4.77 (m, 2H), 1.40 (dd, J_{H-H}=6.2 Hz, J_{H-H}=6.2 Hz, 12H). ^{13}C NMR ($CDCl_3$) δ: 165.0 (d, J_{P-C}=12.4 Hz, C═O), 150.4, 148.5 (d, J_{P-C}=6.5 Hz), 133.8 (d, J_{P-C}=19.5 Hz), 130.6, 129.5, 129.3, 128.8, 126.2, 124.3, 121.2, 71.9 (d, J_{P-C}=5.6 Hz), 24.1 (d, J_{P-C}=3.8 Hz), 23.8 (d, J_{P-C}=5.2 Hz). ^{31}P NMR ($CDCl_3$) δ: 10.9. HRMS (ESI) *m/z*: 389.1514 $[M+H]^+$ (calcd for $C_{21}H_{26}O_5P^+$ 389.1512).

*4.2.2. (E)-Phenyl 2-(diisopropoxyphosphoryl)-3-(4-fluorophenyl)acrylate (**3b**).* 99.9 mg (yield 95%); Reddish-brown viscous liquid. IR (KBr) ν(cm^{-1}): 2981, 2935 (−CH_3), 1747 (C═O), 1601, 1510 (Ar−), 1254 (P═O), 1174 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.78 (d, J_{P-H}=23.8 Hz, 1H), 7.58–7.54 (m, 2H), 7.39 (t, J_{H-H}=7.6 Hz, 2H), 7.25 (t, J_{H-H}=7.5 Hz, 1H), 7.13–7.06 (m, 4H), 4.87–4.76 (m, 2H), 1.42 (d, J_{H-H}=6.2 Hz, 6H), 1.38 (d, J_{H-H}=6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.8 (d, J_{P-C}=12.1 Hz), 153.9 (d, J_{F-C}=251.0 Hz), 150.3, 147.4 (d, J_{P-C}=6.6 Hz), 131.5 (d, J_{F-C}=8.9 Hz), 129.9 (dd, J_{F-C}=3.5 Hz, J_{P-C}=20.2 Hz), 129.5, 126.2, 124.9 (d, J_{P-C}=180.2 Hz), 121.1, 115.9 (d, J_{F-C}=21.8 Hz), 71.9 (d, J_{P-C}=5.5 Hz), 24.0 (d, J_{P-C}=3.9 Hz), 23.8 (d,



Scheme 3. Proposed reaction mechanism.



Scheme 4. Energy profiles on the competing reaction pathways via transition states TS1α and TS1β.

J_{P-C}=5.2 Hz). ^{31}P NMR ($CDCl_3$) δ: 15.1. ^{19}F NMR ($CDCl_3$) δ: −110.2. HRMS (ESI) *m*/*z*: 407.1421 $[M+H]^+$ (calcd for $C_{21}H_{25}FO_5P^+$ 407.1418).

*4.2.3. (E)-Phenyl 3-(4-chlorophenyl)-2-(diisopropoxyphosphoryl)acrylate (**3c**).* 97.1 mg (yield 92%); *Brownish yellow crystal*, mp 60–61 °C. IR (KBr) ν(cm^{-1}): 2979, 2933 (−CH_3), 1745 (C═O), 1591, 1491 (Ar−), 1254 (P═O), 1173 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.75 (d, J_{P-H}=23.7 Hz, 1H), 7.49 (d, J_{H-H}=8.5 Hz, 2H), 7.41–7.38 (m, 4H), 7.27–7.23 (m, 1H), 7.06 (d, J_{H-H}=8.5 Hz, 2H), 4.85–4.77 (m, 2H), 1.41 (d, J_{H-H}=6.2 Hz, 6H), 1.38 (d, J_{H-H}=6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.7 (d, J_{P-C}=12.2 Hz), 150.3, 147.1 (d, J_{P-C}=6.6 Hz), 136.7, 132.1 (d, J_{P-C}=19.9 Hz), 130.6, 129.6, 129.0, 126.2, 125.8 (d, J_{P-C}=179.9 Hz), 121.1, 72.0 (d, J_{P-C}=5.5 Hz), 24.0 (d, J_{P-C}=3.8 Hz), 23.8 (d, J_{P-C}=5.2 Hz). ^{31}P NMR ($CDCl_3$) δ: 10.5. HRMS (ESI) *m*/*z*: 423.1125 $[M+H]^+$ (calcd for $C_{21}H_{25}ClO_5P^+$ 423.1123).

*4.2.4.(E)-Phenyl 2-(diisopropoxyphosphoryl)-3-(4-nitrophenyl)acrylate (**3d**).* 92.0 mg (yield 85%); *Reddish*-brown viscous liquid. IR (KBr) ν(cm^{-1}): 2981, 2930 (−CH_3), 1747 (C═O), 1591, 1523 (Ar−), 1255 (P═O), 1176 (P−O). ^{1}H NMR ($CDCl_3$) δ: 8.27 (d, J_{P-H}=8.7 Hz, 2H), 7.85 (d, J_{H-H}=23.5 Hz, 1H), 7.69 (d, J_{H-H}=8.7 Hz, 2H), 7.40 (d, J_{H-H}=7.7 Hz, 2H), 7.27 (d, J_{H-H}=9.2 Hz, 1H), 7.02 (d, J_{H-H}=7.6 Hz, 1H), 4.88–4.80 (m, 2H), 1.43 (d, J_{H-H}=6.2 Hz, 6H), 1.40 (d, J_{H-H}=6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.0 (d, J_{P-C}=11.7 Hz), 150.1, 148.5, 145.7 (d, J_{P-C}=6.6 Hz), 140.0 (d, J_{P-C}=19.8 Hz), 129.8 (d, J_{P-C}=1.5 Hz), 129.7 (d, J_{P-C}=178.6 Hz), 129.7, 126.5, 123.9, 120.9, 72.4 (d, J_{P-C}=5.8 Hz), 24.1 (d, J_{P-C}=4.1 Hz), 23.8 (d, J_{P-C}=5.1 Hz). ^{31}P NMR ($CDCl_3$) δ: 9.1. HRMS (ESI) *m*/*z*: 434.1365 $[M+H]^+$ (calcd for $C_{21}H_{25}NO_7P^+$ 434.1363).

*4.2.5. (E)-Phenyl 2-(diisopropoxyphosphoryl)-3-(p-tolyl)acrylate (**3e**).* 72.4 mg (yield 72%); Brown yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2979, 2935 (−CH_3), 1747 (C═O), 1589, 1489 (Ar−), 1255 (P═O), 1176 (P−O). ^{1}H NMR ($CDCl_3$) δ: 8.05 (d, J_{P-H}=22.8 Hz, 1H), 7.40 (d, J_{H-H}=7.5 Hz, 1H), 7.30 (t, J_{H-H}=7.7 Hz, 3H), 7.23–7.20 (m, 2H), 7.17 (t, J_{H-H}=7.5 Hz, 1H), 6.86 (d, J_{H-H}=8.6 Hz, 2H), 4.88–4.80 (m, 2H), 2.40 (s, 3H), 1.41 (t, J_{H-H}=6.4 Hz, 12H). ^{13}C NMR ($CDCl_3$) δ: 164.6 (d, J_{P-C}=13.8 Hz), 150.3, 149.0 (d, J_{P-C}=6.3 Hz), 137.0, 133.9 (d, J_{P-C}=18.5 Hz), 130.2 (d, J_{P-C}=39.7 Hz), 127.9 (d, J_{P-C}=1.9 Hz), 127.1 (d, J_{P-C}=180.6 Hz), 126.0 (d, J_{P-C}=8.3 Hz), 121.2, 71.8 (d, J_{P-C}=5.6 Hz), 24.0 (d, J_{P-C}=3.9 Hz), 23.8 (d, J_{P-C}=5.0 Hz), 19.9. ^{31}P NMR ($CDCl_3$) δ: 10.2. HRMS (ESI) *m*/*z*: 403.1670 $[M+H]^+$ (calcd for $C_{22}H_{28}O_5P^+$ 403.1669).

*4.2.6. (E)-Phenyl 2-(diisopropoxyphosphoryl)-3-(3-methoxyphenyl) acrylate (**3f**).* 78.4 mg (yield 75%); Brown yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2979, 2935 (−CH_3), 1745 (C═O), 1589, 1489 (Ar−), 1255 (P═O), 1176 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.77 (d, J_{P-H}=23.7 Hz, 1H), 7.37 (t, J_{H-H}=7.9 Hz, 2H), 7.33 (t, J_{H-H}=7.8 Hz, 1H), 7.23 (t, J_{H-H}=7.4 Hz, 1H), 7.13 (d, J_{H-H}=7.6 Hz, 1H), 7.05 (d, J_{H-H}=8.3 Hz, 3H), 6.96 (dd, J_{H-H}=8.3 Hz, J_{H-H}=1.6 Hz, 1H), 4.85–4.77 (m, 2H), 3.77 (s, 3H), 1.41 (d, J_{H-H}=6.2 Hz, 6H), 1.38 (d, J_{H-H}=6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 165.0 (d, J_{P-C}=12.6 Hz), 159.7, 150.4, 148.2 (d, J_{P-C}=6.4 Hz), 135.0 (d, J_{P-C}=19.8 Hz), 129.8, 129.5, 126.2, 125.6 (d, J_{P-C}=179.6 Hz), 121.6, 121.2, 116.5, 114.3, 71.9 (d, J_{P-C}=5.4 Hz), 55.3, 24.1 (d, J_{P-C}=3.9 Hz), 23.8 (d, J_{P-C}=5.2 Hz). ^{31}P NMR ($CDCl_3$) δ: 10.8. HRMS (ESI) *m*/*z*: 419.1622 $[M+H]^+$ (calcd for $C_{22}H_{28}O_6P^+$ 419.1618).

*4.2.7. (E)-Phenyl 2-(diisopropoxyphosphoryl)-3-(4-methoxyphenyl) acrylate (**3g**).* 85.7 mg (yield 82%); Light yellow crystal, mp 100–101 °C. IR (KBr) ν(cm^{-1}): 2978, 2936 (−CH_3), 1741 (C═O), 1601, 1512 (Ar−), 1267 (P═O), 1171 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.69 (d, J_{P-H}=24.0 Hz, 1H), 7.50 (d, J_{H-H}=8.8 Hz, 2H), 7.34 (t, J_{H-H}=7.8 Hz, 2H), 7.18 (t, J_{H-H}=7.4 Hz, 1H), 7.07 (t, J_{H-H}=7.7 Hz, 2H), 6.86 (d, J_{H-H}=8.8 Hz, 2H), 4.79–4.71 (m, 2H), 3.75 (s, 3H), 1.36 (d, J_{H-H}=6.2 Hz, 6H), 1.32 (d, J_{H-H}=6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 165.3 (d, J_{P-C}=12.5 Hz), 150.5, 148.5 (d, J_{P-C}=6.7 Hz), 131.6, 129.5, 126.2 (d, J_{P-C}=1.3 Hz), 126.1, 121.6 (d, J_{P-C}=181.7 Hz), 121.3, 114.2, 71.6 (d, J_{P-C}=5.6 Hz), 55.3, 24.0 (d, J_{P-C}=4.0 Hz), 23.7 (d, J_{P-C}=5.3 Hz). ^{31}P NMR ($CDCl_3$) δ: 12.0. HRMS (ESI) *m*/*z*: 419.1620 $[M+H]^+$ (calcd for $C_{22}H_{28}O_6P^+$ 419.1618).

*4.2.8. (E)-Methyl 2-(diisopropoxyphosphoryl)-3-phenylacrylate (**3h**).* 71.7 mg (yield 88%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2979, 2937 (−CH_3), 1728 (C═O), 1612, 1375 (Ar−), 1254 (P═O), 1047 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.61 (d, J_{P-H}=24.0 Hz, 1H), 7.37–7.32 (m, 5H), 4.76–4.66 (m, 2H), 3.74 (s, 3H), 1.34 (d, J_{H-H}=6.2 Hz, 6H), 1.30 (d, J_{H-H}=6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 167.0 (d, J_{P-C}=12.4 Hz), 147.7 (d, J_{P-C}=6.4 Hz), 133.7 (d, J_{P-C}=19.8 Hz), 130.3, 129.0, 128.7, 125.4 (d, J_{P-C}=179.4 Hz), 71.6 (d, J_{P-C}=5.3 Hz), 52.3, 24.0 (d, J_{P-C}=3.7 Hz), 23.6 (d, J_{P-C}=6.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 11.3. HRMS (ESI) *m*/*z*: 327.1358 $[M+H]^+$ (calcd for $C_{16}H_{24}O_5P^+$ 327.1356).

*4.2.9. (E)-Diethyl (3-oxo-1-phenylbut-1-en-2-yl)phosphonate (**3i**).* 36.7 mg (yield 52%); Brownish yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2985, 2908 (−CH_3, −CH_2), 1701 (C═O), 1606, 1448 (Ar−), 1252 (P═O), 1051 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.57 (d, J_{P-H}=25.6 Hz, 1H), 7.41–7.30 (m, 5H), 4.23–4.16 (m, 4H), 2.27 (s, 3H), 1.37 (t, J_{H-H}=7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 203.2 (d, J_{P-C}=8.5 Hz), 145.0 (d, J_{P-C}=5.8 Hz), 133.9 (d, J_{P-C}=169.7 Hz), 133.6 (d, J_{P-C}=21.3 Hz), 130.3, 129.2 (d, J_{P-C}=1.0 Hz), 128.9, 62.7 (d, J_{P-C}=5.7 Hz), 31.1 (d, J_{P-C}=2.0 Hz), 16.2 (d, J_{P-C}=6.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 13.9. HRMS (ESI) *m*/*z*: 283.1095 $[M+H]^+$ (calcd for $C_{14}H_{20}O_4P^+$ 283.1094).

*4.2.10. (E)-Diisopropyl (1-nitro-2-phenylvinyl)phosphonate (**3j**).* 42.2 mg (yield 63%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2978, 2933 (−CH_3), 1614, 1450 (Ar−), 1246 (P═O), 1105 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.53–7.43 (m, 3H), 7.39–7.36 (m, 3H), 6.27 (t, J_{H-H}=17.4 Hz, 1H), 4.77–4.66 (m, 2H), 1.37 (d, J_{H-H}=6.2 Hz, 6H), 1.30 (d, J_{H-H}=6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 147.7 (d, J_{P-C}=6.8 Hz), 135.0 (d, J_{P-C}=23.2 Hz), 130.0, 128.8, 127.6, 115.6 (d, J_{P-C}=190.9 Hz), 70.4 (d, J_{P-C}=5.6 Hz), 24.1 (d, J_{P-C}=4.2 Hz), 24.0 (d, J_{P-C}=4.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 17.5. HRMS (ESI) *m*/*z*: 269.1303 $[M+H]^+$ (calcd for $C_{14}H_{22}O_3P^+$ 269.1301).

*4.2.11. (E)-Phenyl 2-(dimethoxyphosphoryl)-3-phenylacrylate (**3l**).* 43.2 mg (yield 52%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2954, 2918, 2850 (−CH_3), 1743 (C═O), 1591, 1491, 1456 (Ar−), 1259 (P═O), 1178 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.82 (d, J_{P-H}=24.0 Hz, 1H), 7.56 (dd, J_{H-H}=6.6 Hz, J_{H-H}=1.8 Hz, 2H), 7.44–7.36 (m, 5H), 7.23 (d, J_{H-H}=7.5 Hz, 1H), 7.06 (t, J_{H-H}=1.0 Hz, 2H), 3.88 (d, J_{P-H}=4.6 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.8 (d, J_{P-C}=13.1 Hz, C═O), 150.3, 150.1 (d, J_{P-C}=6.0 Hz), 133.4 (d, J_{P-C}=19.8 Hz), 130.9, 129.5, 129.4, 129.4, 128.8, 126.3, 122.6 (d, J_{P-C}=180.2 Hz), 53.3 (d, J_{P-C}=5.2 Hz). ^{31}P NMR ($CDCl_3$) δ: 16.4. HRMS (ESI) *m*/*z*: 333.0888 $[M+H]^+$ (cald for $C_{17}H_{18}O_5P^+$ 333.0886).

*4.2.12. (E)-Phenyl 2-(diethoxyphosphoryl)-3-phenylacrylate (**3m**).* 56.7 mg (yield 63%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2952, 2924, 2850 (−CH_3, −CH_2), 1743 (C═O), 1483, 1458 (Ar−), 1255 (P═O), 1176 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.81 (d, J_{P-H}=23.8 Hz, 1H), 7.56 (dd, J_{H-H}=5.7 Hz, J_{H-H}=1.9 Hz, 2H), 7.44–7.37 (m, 5H), 7.26 (d, J_{H-H}=6.8 Hz, 1H), 7.05 (dd, J_{H-H}=8.7 Hz, J_{H-H}=1.2 Hz, 2H), 4.29–4.21 (m, 4H), 1.40 (t, J_{P-H}=7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.9 (d, J_{P-C}=12.4 Hz, C═O), 150.3, 149.3 (d, J_{P-C}=6.4 Hz), 133.5 (d, J_{P-C}=19.6 Hz), 130.7, 129.5, 129.4, 128.8,

126.3, 123.8 (d, J_{P-C}=178.9 Hz), 121.2, 63.0 (d, J_{P-C}=5.2 Hz), 16.3 (d, J_{P-C}=6.7 Hz). ^{31}P NMR ($CDCl_3$) δ: 13.4. HRMS (ESI) *m/z*: 361.1201 $[M+H]^+$ (cald for $C_{19}H_{22}O_5P^+$ 361.1199).

*4.2.13. (E)-Phenyl 2-(dipropoxyphosphoryl)-3-phenylacrylate (**3n**).* 58.2 mg (yield 60%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2970, 2918, 2870 (−CH_3, −CH_2), 1743 (C=O), 1491, 1456 (Ar−), 1250 (P=O), 1174 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.81 (d, J_{P-H}=23.8 Hz, 1H), 7.56−7.54 (m, 2H), 7.43−7.36 (m, 5H), 7.24 (t, J_{H-H}=7.4 Hz, 1H), 7.06−7.03 (m, 2H), 4.17−4.10 (m, 4H), 1.81−1.72 (m, 4H), 0.98 (t, J_{H-H}=7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.9 (d, J_{P-C}=12.9 Hz, C=O), 150.4, 149.2 (d, J_{P-C}=6.1 Hz), 133.6 (d, J_{P-C}=19.7 Hz), 130.7, 129.5, 129.4, 128.8, 126.2, 123.9 (d, J_{P-C}=179.5 Hz), 121.2, 68.3 (d, J_{P-C}=5.7 Hz), 23.8 (d, J_{P-C}=6.6 Hz), 10.0. ^{31}P NMR ($CDCl_3$) δ: 12.9. HRMS (ESI) *m/z*: 389.1516 $[M+H]^+$ (calcd for $C_{21}H_{26}O_5P^+$ 389.1512).

*4.2.14. (E)-Phenyl 2-(diisobutoxyphosphoryl)-3-phenylacrylate (**3o**).* 66.6 mg (yield 64%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2958, 2924 (−CH_3, −CH_2), 1745 (C=O), 1475, 1460 (Ar−), 1254 (P=O), 1174 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.82 (d, J_{P-H}=23.8 Hz, 1H), 7.56−7.54 (m, 2H), 7.43−7.36 (m, 5H), 7.24 (d, J_{H-H}=7.5 Hz, 1H), 7.04 (d, J_{H-H}=7.7 Hz, 2H), 3.97−3.93 (m, 4H), 2.02 (t, J_{H-H}=6.6 Hz, 2H), 0.98 (d, J_{H-H}=2.4 Hz, 6H), 0.97 (d, J_{H-H}=2.4 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.8 (d, J_{P-C}=13.1 Hz, C=O), 150.3, 149.4 (d, J_{P-C}=6.2 Hz), 133.6 (d, J_{P-C}=19.6 Hz), 130.7, 129.5, 129.4, 128.8, 126.2, 123.7 (d, J_{P-C}=180.9 Hz), 121.2, 72.7 (d, J_{P-C}=6.7 Hz), 29.2 (d, J_{P-C}=3.7 Hz), 18.7. ^{31}P NMR ($CDCl_3$) δ: 12.9. HRMS (ESI) *m/z*: 417.1825 $[M+H]^+$ (calcd for $C_{23}H_{30}O_5P^+$ 417.1825).

*4.2.15. (E)-Phenyl 2-(bis(benzyloxy)phosphoryl)-3-phenylacrylate (**3p**).* 82.3 mg (yield 68%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3014, 2970 (−CH_2), 1724 (C=O), 1504, 1458 (Ar−), 1288 (P=O), 1192 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.83 (d, J_{P-H}=24.3 Hz, 1H), 7.51−7.49 (m, 2H), 7.42−7.39 (m, 7H), 7.34−7.29 (m, 9H), 6.85 (d, J_{H-H}=7.5 Hz, 2H), 5.20 (d, J_{P-H}=7.8 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ: 164.7 (d, J_{P-C}=13.3 Hz, C=O), 150.2, 150.1 (d, J_{P-C}=6.4 Hz), 135.8 (d, J_{P-C}=7.2 Hz), 133.5 (d, J_{P-C}=20.2 Hz), 130.8, 129.5 (d, J_{P-C}=1.3 Hz), 129.4, 128.8, 128.6, 128.5, 128.1, 126.2, 123.5 (d, J_{P-C}=181.5 Hz), 121.2, 68.3 (d, J_{P-C}=5.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 14.1. HRMS (ESI) *m/z*: 485.1510 $[M+H]^+$ (calcd for $C_{29}H_{26}O_5P^+$ 485.1512).

*4.2.16. (E)-Phenyl 2-(diphenylphosphoryl)-3-phenylacrylate (**3q**).* 48.8 mg (yield 46%); Brown red viscous liquid. IR (KBr) ν(cm^{-1}): 1747 (C=O), 1591, 1489 (Ar−), 1265 (P=O), 1176 (P−O). ^{1}H NMR ($CDCl_3$) δ: 8.05 (d, J_{P-H}=19.8 Hz, 1H), 7.95−7.90 (m, 4H), 7.60−7.55 (m, 4H), 7.51−7.47 (m, 4H), 7.41 (t, J_{H-H}=3.4 Hz, 3H), 7.21 (t, J_{H-H}=8.0 Hz, 2H), 7.11 (t, J_{H-H}=7.4 Hz, 1H), 6.49 (d, J_{H-H}=7.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 165.9 (d, J_{P-C}=14.8 Hz, C=O), 149.9, 149.7 (d, J_{P-C}=4.5 Hz), 134.0 (d, J_{P-C}=14.5 Hz), 132.4 (d, J_{P-C}=2.7 Hz), 132.4, 132.3, 131.2 (d, J_{P-C}=107.4 Hz), 130.7, 128.8, 128.7, 128.6, 126.2, 120.9. ^{31}P NMR ($CDCl_3$) δ: 25.6. HRMS (ESI) *m/z*: 425.1298 $[M+H]^+$ (calcd for $C_{27}H_{22}O_3P^+$ 425.1301).

*4.2.17. (E)-Phenyl 2-(diethoxyphosphoryl)-3-(o-tolyl)acrylate (**3r**).* 61.7 mg (yield 66%); Brownish yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3057 (−CH_3, −CH_2), 1736 (C=O), 1589, 1491, 1437 (Ar−), 1274 (P=O), 1119 (P−O). ^{1}H NMR ($CDCl_3$) δ: 8.05 (d, J_{P-H}=22.8 Hz, 1H), 7.41 (d, J_{H-H}=7.5 Hz, 1H), 7.33−7.27 (m, 3H), 7.24−7.16 (m, 3H), 6.87 (d, J_{H-H}=8.5 Hz, 2H), 4.31−4.23 (m, 4H), 2.40 (s, 3H), 1.41 (t, J_{H-H}=7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.6 (d, J_{P-C}=14.3 Hz), 150.3, 149.8 (d, J_{P-C}=6.3 Hz), 137.0, 133.7 (d, J_{P-C}=18.7 Hz), 130.3 (d, J_{P-C}=28.1 Hz), 129.4, 127.9 (d, J_{P-C}=1.9 Hz), 125.7 (d, J_{P-C}=179.5 Hz), 126.0 (d, J_{P-C}=13.1 Hz), 121.2, 63.0 (d, J_{P-C}=5.4 Hz), 19.8, 16.3 (d, J_{P-C}=6.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 12.7. HRMS (ESI) *m/z*: 375.1354 $[M+H]^+$ (calcd for $C_{20}H_{24}O_5P^+$ 375.1356).

*4.2.18. (E)-Phenyl 3-(4-chlorophenyl)-2-(diethoxyphosphoryl)acrylate (**3s**).* 69.9 mg (yield 71%); Brownish yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2983, 2929 (−CH_3, −CH_2), 1745 (C=O), 1616, 1591, 1491 (Ar−), 1255 (P=O), 1174 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.75 (d, J_{P-H}=23.8 Hz, 1H), 7.49 (d, J_{H-H}=8.5 Hz, 2H), 7.42−7.38 (m, 4H), 7.27−7.24 (m, 1H), 7.06 (d, J_{H-H}=8.5 Hz, 2H), 4.29−4.21 (m, 4H), 1.40 (d, J_{H-H}=7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 164.7 (d, J_{P-C}=12.4 Hz), 150.2, 147.8 (d, J_{P-C}=6.2 Hz), 136.8, 131.9 (d, J_{P-C}=20.1 Hz), 130.6, 129.6, 129.1, 126.4, 124.5 (d, J_{P-C}=178.7 Hz), 121.1, 63.0 (d, J_{P-C}=5.3 Hz), 16.3 (d, J_{P-C}=6.6 Hz). ^{31}P NMR ($CDCl_3$) δ: 12.9. HRMS (ESI) *m/z*: 395.0813 $[M+H]^+$ (calcd for $C_{19}H_{21}ClO_5P^+$ 395.0810).

*4.2.19. (E)-Methyl 2-(dimethoxyphosphoryl)-3-phenylacrylate (**3t**).* 58.1 mg (yield 86%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2954, 2850 (−CH_3), 1726 (C=O), 1612, 1435 (Ar−), 1257 (P=O), 1057 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.68 (d, J_{P-H}=24.2 Hz, 1H), 7.41−7.38 (m, 5H), 3.84 (s, 3H), 3.81 (d, J_{P-H}=6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 166.7 (d, J_{P-C}=12.9 Hz), 149.3 (d, J_{P-C}=6.1 Hz), 133.4 (d, J_{P-C}=19.8 Hz), 130.7, 129.1 (d, J_{P-C}=1.1 Hz), 128.7, 122.6 (d, J_{P-C}=180.2 Hz), 53.2 (d, J_{P-C}=5.4 Hz), 52.7. ^{31}P NMR ($CDCl_3$) δ: 16.9. HRMS (ESI) *m/z*: 271.0728 $[M+H]^+$ (calcd for $C_{12}H_{16}O_5P^+$ 271.0730).

*4.2.20. (E)-Methyl 2-(diethoxyphosphoryl)-3-phenylacrylate (**3u**).* 44.7 mg (yield 60%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2983, 2906 (−CH_3, −CH_2), 1726 (C=O), 1612, 1433 (Ar−), 1254 (P=O), 1053 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.63 (d, J_{P-H}=24.1 Hz, 1H), 7.39−7.32 (m, 5H), 4.21−4.11 (m, 4H), 3.76 (s, 3H), 1.34 (t, J_{H-H}=7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 166.9 (d, J_{P-C}=12.8 Hz), 148.5 (d, J_{P-C}=6.3 Hz), 133.5 (d, J_{P-C}=19.9 Hz), 130.5, 129.1, 128.7, 124.9, 123.1, 62.8 (d, J_{P-C}=5.1 Hz), 52.6, 16.2 (d, J_{P-C}=6.6 Hz). ^{31}P NMR ($CDCl_3$) δ: 13.8. HRMS (ESI) *m/z*: 299.1045 $[M+H]^+$ (calcd for $C_{14}H_{20}O_5P^+$ 299.1043).

*4.2.21. (E)-Dimethyl (3-oxo-1-phenylbut-1-en-2-yl)phosphonate (**3v**).* 52.1 mg (yield 82%); Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2954, 2850 (−CH_3, −CH_2), 1703 (C=O), 1606, 1448 (Ar−), 1254 (P=O), 1180 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.61 (d, J_{P-H}=25.7 Hz, 1H), 7.41−7.30 (m, 5H), 3.83 (d, J_{P-H}=11.3 Hz, 6H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 203.0 (d, J_{P-C}=8.5 Hz), 145.9 (d, J_{P-C}=5.8 Hz), 133.5 (d, J_{P-C}=11.9 Hz), 133.4, 130.5, 129.3, 128.9, 53.1 (d, J_{P-C}=5.5 Hz), 31.0 (d, J_{P-C}=2.2 Hz). ^{31}P NMR ($CDCl_3$) δ: 16.9. HRMS (ESI) *m/z*: 255.0778 $[M+H]^+$ (calcd for $C_{12}H_{16}O_4P^+$ 255.0781).

*4.2.22. (E)-Dimethyl styrylphosphonate (**3w**).* 37.1 mg (yield 70%); Yellow viscous liquid. IR (KBr) ν(cm^{-1}): 2952, 2850 (−CH_3), 1616, 1448 (Ar−), 1250 (P=O), 1053 (P−O). ^{1}H NMR ($CDCl_3$) δ: 7.58−7.48 (m, 3H), 7.40−7.29 (m, 3H), 6.23 (t, J_{H-H}=17.7 Hz, 1H), 3.77 (d, J_{P-H}=11.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 149.6 (d, J_{P-C}=6.6 Hz), 134.6 (d, J_{P-C}=23.2 Hz), 130.4, 128.8, 127.7, 112.3 (d, J_{P-C}=191.1 Hz), 52.4 (d, J_{P-C}=5.7 Hz). ^{31}P NMR ($CDCl_3$) δ: 22.6. HRMS (ESI) *m/z*: 213.0677 $[M+H]^+$ (calcd for $C_{10}H_{14}O_3P^+$ 213.0675).

Acknowledgements

We gratefully acknowledge the National Natural Science Foundation of China (No. 21302042 and 21172055), Department of Henan Province Natural Science and Technology Foundation (No. 142102210410), Natural Science Foundation in Henan Province Department of Education (No. 14B150053), the Program for Innovative Research Team from Zhengzhou (No. 131PCXTD605), and

Natural Science Foundation from Technology Bureau of Zhengzhou (No. 20130883).

Supplementary data

Supplementary data (^{1}H, ^{13}C and ^{31}P NMR spectra for products and computational methods) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.04.034.

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