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Hydroxyphosphinylation Reaction of 3-Cyclopropylideneprop-2-en-1-ones via C−P σ-Bond Cleavage

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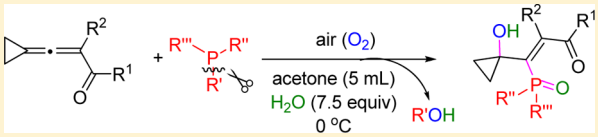
Supporting Information

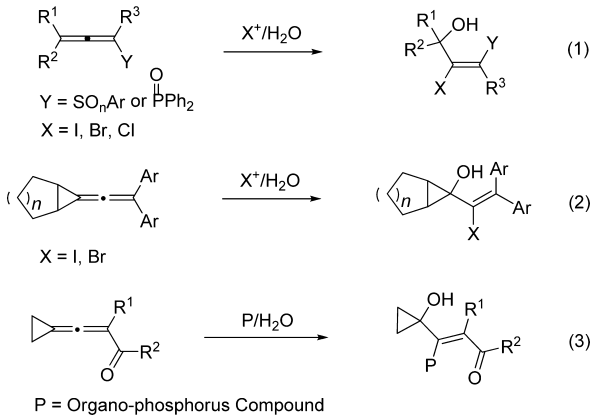
ABSTRACT: An unexpected hydroxyphosphinylation of 3-cyclopropylideneprop-2-en-1-ones with phosphines has been observed. This method provides a unique regio- and stereoselective synthesis of highly functionalized 1-dialkylphinyl-3-oxo-(1*Z*)-alkenyl cyclopropanols with important potentials. The reaction displays an unusual mechanistic feature—a highly selective cleavage of C−P σ bonds in phosphines.



INTRODUCTION

The addition reactions of a carbon−carbon multiple bond constitute highly synthetically versatile processes. Two identical or different functionalities, which can undergo a multitude of further synthetic transformations, are added to the unsaturated moiety in a single step.[1] In the past few decades, much attention has been paid to the halohydroxylation reaction of allenes because it is a powerful method for introducing the halogen and hydroxyl groups to form β-halogen-substituted alcohols.[2] Previously, Ma[3] has reported that attaching a heteroatom such as sulfur or phosphorus adjacent to allenes would be an effective solution and a series of corresponding 2-halogen-substituted allylic alcohols could be regio- and stereoselectively synthesized via the halohydroxylation of the substituted allenes (Scheme 1, eq 1). In this case, we have presented a comprehensive study of the halohydroxylation reaction of vinylidenecyclopropanes that provides direct synthetic access to vinylbicyclo[(*n*+2).1.0]alkanols with excellent regio- and diastereoselectivity[4] (Scheme 1, eq 2). However, to best of our knowledge, reports on the addition reactions of allenes with the introduction of the hydroxyl group and organophosphorus group at the same time are limited. Meanwhile, the 3-cyclopropylideneprop-2-en-1-ones,[5] which contain the highly strained cyclopropyl ring and carboxyl group adjacent to the two ends of cumulated C═C bonds, are a kind of highly activated analogue of allenes. In the presence of the carboxyl group adjacent to the allene group, the substrates have great potential to react with organophosphorus compounds. Thus, we turned our effort toward such a "phosphorus-hydroxylation" reaction of 3-cyclopropylideneprop-2-en-1-ones (Scheme 1, eq 3).

Scheme 1. Reported Halohydroxylation Reactions and Our Concept of the "Phosphorus-Hydroxylation" Reaction



On the other hand, the selective cleavage of an unactivated element−carbon bond has always been an attractive topic in organic synthesis.[6] Several reactions involving the cleavage of C−P bonds have been well reported.[7] In particular, the C−P bond cleavage in tertiary phosphines has attracted considerable interest because they are important ligands for transition metals and are versatile intermediates in organic synthesis.[8] Much progress on C−P activation with transition metals in tertiary phosphines has been achieved in the past few decades:[9] For example, Chan and co-workers have reported a catalytic user-friendly phosphination using triarylphosphines (Scheme 2, eq 1);[9a] Jackson and co-workers have established the preparation of diphenyl-substituted phosphines using alkali metals in silica gel (M-SG) (Scheme 2, eq 2).[9b] However, very few examples of direct cleavage of C−P σ bonds that form phosphorus-containing compounds[10] without metals have been reported because of the relatively strong C−P σ bond.[11] Herein we disclose our recent unexpected observations on the hydroxyphosphinylation reaction of 3-cyclopropylideneprop-2-en-1-

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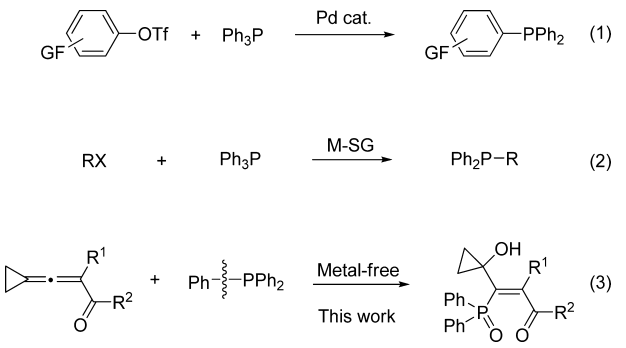
Scheme 2. Reported C−P Cleavage Reactions and Our Observations on Metal-Free C−P Cleavage Reactions

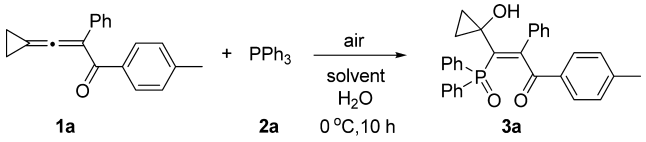


ones for introducing the hydroxyl group and phosphorus group via C−P bond cleavage (Scheme 2, eq 3).

RESULTS AND DISCUSSION

Initially, the reaction of **1a** with 1.5 equiv of triphenylphosphine (**2a**) in the presence of 2.5 equiv of H_2O in acetone in open air afforded the unknown product **3a** (Table 1, entry 1). Through

Table 1. Optimization of the Reaction Conditions for the Formation of 3a[a]



1a 2a 3a

entry	amt of PPh_3 (equiv)	amt of H_2O (equiv)	solvent	yield of **3a** (%)[b]
1	1.5	2.5	acetone	60
2	**1.5**	**7.5**	**acetone**	**74**
3	1.5	10	acetone	74
4	1.0	7.5	acetone	46[c]
5	2.0	7.5	acetone	73
6	1.5	7.5	DCM	69
7	1.5	7.5	CH_3CN	72
8[d]	1.5	7.5	toluene	29
9	1.5	7.5	CH_3OH	0[e]
10[f]	1.5	7.5	acetone	52
11[g]	1.5	7.5	acetone	complex
12[h]	1.5	7.5	acetone	62
13[i]	1.5	7.5	acetone	trace

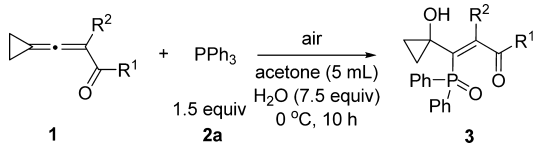
[a]The reaction was carried out using **1a** (0.15 mmol) in 5 mL of solvent in open air. [b]Isolated yields. [c]17% of **1a** was recovered. [d]Reaction time 36 h. [e]Unknown products were formed. [f]The reaction was conducted at room temperature. [g]The reaction was conducted under reflux. [h]The reaction was conducted under an oxygen atmosphere for 4 h. [i]The reaction was conducted under a nitrogen atmosphere.

spectroscopic (^1H and ^{13}C NMR, MS) and X-ray diffraction analysis (Figure S1, Supporting Information), we identified that the product **3a** contains a vinylcyclopropanol unit with a phosphoryl group attached to the C=C bond, showing an exclusive *Z* selectivity; thus, the reaction showed an unexpected aryl−P bond cleavage with unique regio- and stereoselectivity.

Optimization of the Hydroxyphosphinylation Reaction. Efforts were then made to optimize the reaction conditions to improve the yield of **3a**. Typical results of the reaction are summarized in Table 1. The yield was improved to 74% when 7.5 equiv of H_2O was used; a higher loading of H_2O failed to give a higher yield (Table 1, entries 2 and 3). A 1.5 equiv amount of triphenylphosphine is necessary (Table 1, entries 2, 4, and 5). The reaction could also be conducted in DCM and CH_3CN, affording **3a** in good yields (Table 1, entries 6 and 7); however, the reaction performed poorly in nonpolar toluene (Table 1, entry 8); CH_3OH turned out to be totally ineffective, probably due to the nucleophilic solvent leading to other reactions (Table 1, entry 9). The yield of **3a** dropped at a higher temperature (Table 1, entries 10 and 11). Moreover, using pure oxygen instead of air led to a faster reaction, albeit with a lower yield of **3a** (Table 1, entry 12). When the reaction was conducted under an N_2 atmosphere, only a trace amount of **3a** was formed (Table 1, entry 13), indicating that the oxygen in the air must play an important role in this reaction. Finally, the best conditions are defined as follows: reaction in acetone at 0 °C using 1.5 equiv of triphenylphosphine (**2a**) and 7.5 equiv of H_2O in open air (Table 1, entry 2).

Scope of the Hydroxyphosphinylation Reaction. With the optimized conditions in hand, the scope of the reaction of a variety of compounds **1** with triphenylphosphine (**2a**) was examined. The results summarized in Table 2 show that

Table 2. Scope of the Reaction of Various Compounds 1 with Triphenylphosphine 2a for the Formation of 3[a]



1 2a 3

entry	R^1, R^2 for **1**	yield of **3** (%)[b]
1	4-MeC_6H_4, Ph (**1a**)	74 (**3a**)
2	Ph, Ph (**1b**)	69 (**3b**)
3	4-FC_6H_4, Ph (**1c**)	87 (**3c**)
4	4-BrC_6H_4, Ph (**1d**)	90 (**3d**)
5	4-$MeOC_6H_4$, Ph (**1e**)	73 (**3e**)
6	2-furyl, Ph (**1f**)	56 (**3f**)
7	2-thienyl, Ph (**1g**)	43 (**3g**)
8	4-ClC_6H_4, 2-$MeOC_6H_4$ (**1h**)	57 (**3h**)
9	Ph, 3-MeC_6H_4 (**1i**)	72 (**3i**)
10	Ph, 4-$MeOC_6H_4$ (**1j**)	90 (**3j**)
11	Ph, 4-FC_6H_4 (**1k**)	94 (**3k**)
12	Ph, 2-naphthyl (**1l**)	79 (**3l**)

[a]Unless otherwise specified, the reaction was carried out using **1** (0.15 mmol) in presence of 1.5 equiv of PPh_3 and 7.5 equiv of H_2O in 5 mL of acetone in an air atmosphere at 0 °C. [b]Isolated yields.

different products **3** could be obtained smoothly in moderate to high yields. When R^2 is a phenyl group, various useful substituted phenyl (Table 2, entries 1−5) were well tolerated at the R^1 position, with the more electron-deficient **1c,d** affording **3c,d** in higher yields (Table 2, entries 3 and 4); the heteroaromatic substituted **1f,g** also gave the products in moderate yields (Table 2, entries 6 and 7). Moreover, electron-donating groups or electron-withdrawing groups on the aromatic rings and *β*-naphthyl were well tolerated at the R^2 position (Table 2, entries 9−12).

Subsequently, we investigated the scope and limitations of phosphines with substrate **1b** (Table 3). The reaction may be conducted with arylphosphines substituted with electron-

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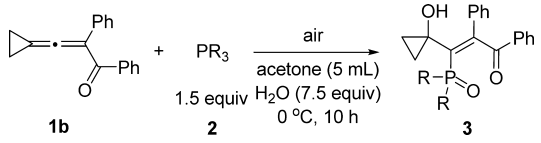
Table 3. Scope of the Reaction of 1b with Phosphines 2 for the Formation of 3[a]



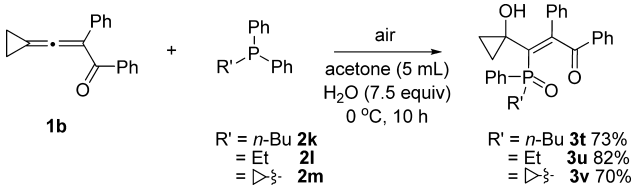
entry	R (2)	yield of 3 (%)[b]
1	4-$MeOC_6H_4$ (**2b**)	80 (**3m**)
2	3,5-$(MeO)_2C_6H_4$ (**2c**)	78 (**3n**)
3	4-FC_6H_4 (**2d**)	50[c] (**3o**)
4	4-ClC_6H_4 (**2e**)	48[c] (**3p**)
5	4-MeC_6H_4 (**2f**)	64 (**3q**)
6	3-MeC_6H_4 (**2g**)	69 (**3r**)
7	2-MeC_6H_4 (**2h**)	NR
8	*n*-Bu (**2i**)	complex
9	2-naphthyl (**2j**)	74 (**3s**)

[a]Unless otherwise specified, the reaction was carried out using **1b** (0.15 mmol) in presence of 1.5 equiv of PR_3 and 7.5 equiv of H_2O in 5 mL of acetone in an air atmosphere at 0 °C. [b]Isolated yields. [c]The reaction was conducted at 0 °C and then at room temperature for 10 h.

donating and electron-withdrawing groups and tri-*β*-naphthylphosphine (Table 3 entries 1–6 and 9). With R being 4-halophenyl, the reaction proceeded at 0 °C and then at room temperature for 10 h to give products **3o,p** in moderate yields (Table 3, entries 3 and 4). When R is a 2-methylphenyl group, no reaction was observed (Table 3, entry 7). Moreover, the reaction gave a complex mixture when applying tri-*n*-butylphosphine (**2i**) (Table 3, entry 8).

In order to find out whether different C–P bonds may be selectively cleaved, the reaction of **1b** with alkyldiarylsubstituted phosphines was also tested. With R′ being *n*-butyl, ethyl, or the cyclopropanyl group, the reaction proceeded smoothly to give the corresponding products **3t–v** in good yields via highly selective cleavage of the phenyl–P bond (Scheme 3).

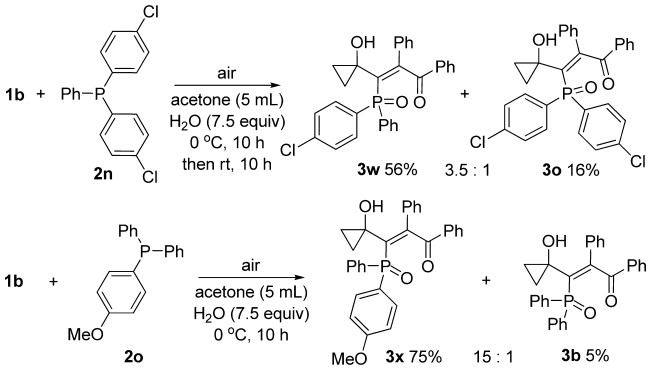
Scheme 3. Highly Selective Hydroxyphosphinylation Reaction of 1b with Akyldiphenylphosphines 2k–m



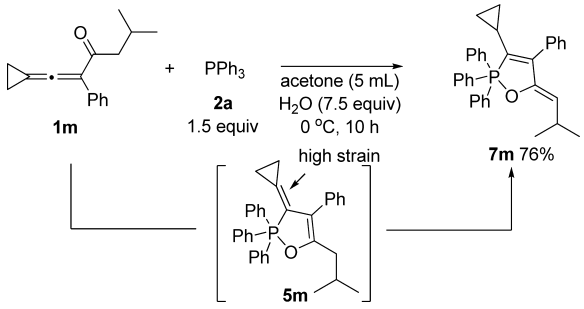
The electronic effect on the selectivity of C–P bond cleavage in this hydroxyphosphinylation reaction was also studied. The reaction of phenylbis(4-chlorophenyl)phosphine (**2n**) with **1b** gave **3w** in 56% yield by selective cleavage of the 4-chlorophenyl–phosphorus bond (Scheme 4). In addition, the reaction of (4-methoxyphenyl)diphenylphosphine (**2o**) with **1b** afforded **3x** via highly selective phenyl–phosphorus bond cleavage in 75% yield together with 5% of product **3b**, cleaving the 4-methoxyphenyl–phosphorus bond (Scheme 4).

Mechanistic Study. The reaction of isobutyl ketone **1m** in the presence of 1.5 equiv of triphenylphosphine (**2a**) in acetone at 0 °C gave the 1,2-oxaphospholene **7m** in 76% yield with high stereoselectivity (Scheme 5). The structure of this product was

Scheme 4. Electronic Effects on the Selectivity of C–P Bond Cleavage in the Hydroxyphosphinylation Reaction



Scheme 5. Reaction of Isobutyl Ketone 1m with Triphenylphosphine 2a



unambiguously established by single-crystal X-ray diffraction analysis (Figure 1), indicating that the product **7m** may be

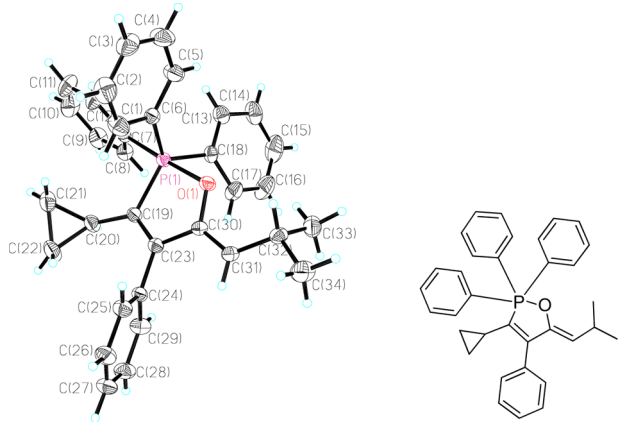


Figure 1. ORTEP representation of **7m**.

formed from the key intermediate 1,2-oxaphospholene **5m** via the C=C bond rearrangement in the presence of a highly strained C=C bond. In addition, we reasoned that the presence of high strain in the C=C bond is also important to the hydroxyphosphinylation reaction.

Finally, we carried out the reaction of **1a** with triphenylphosphine (**2a**) in the presence of $H_2{}^{18}O$ (Scheme 6) and observed the following. (1) The aryl group cleaved from triphenylphosphine was transformed to phenol, which was confirmed by comparison with the standard MS data of phenol, and the yield was calculated with an interior standard. Moreover, 3,5-dimethoxyphenol was isolated in 78% yield when the substrate **1b** was treated with tris(3,5-

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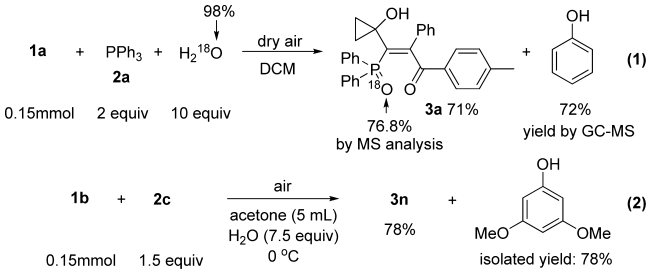
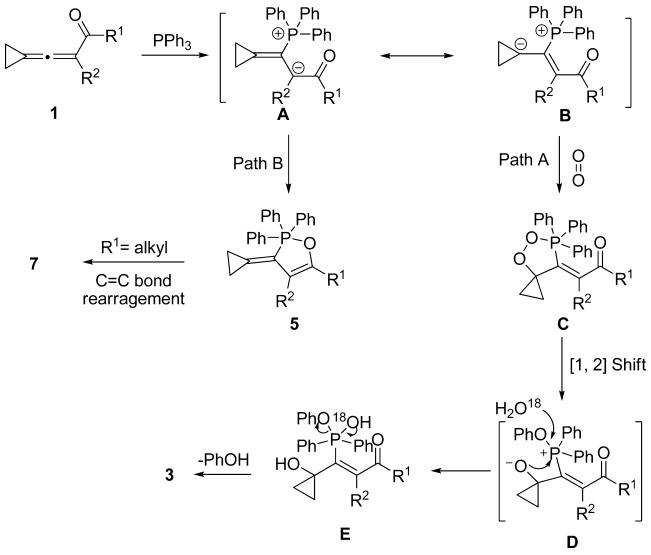
Scheme 6. Mechanistic Study



dimethoxyphenyl)phosphine (**2c**) (Scheme 6, eq 2); (2) **3a**-^{18}O was formed in 71% yield with 76.8% of ^{18}O in the oxygen atom of the phosphoryl group as identified by MS analysis. In addition, there is no incorporation of ^{18}O in the hydroxy group of **3a** and phenol.

On the basis of the above observation, we proposed a plausible mechanism for this reaction (Scheme 7): the reaction

Scheme 7. Plausible Mechanism



starts with an attack of triphenylphosphine at the central allenic carbon atom to form zwitterion **A** and the resonance form **B**.[12] **B** is probably favored due to the release of strain. When R^1 = alkyl, intramolecular nucleophilic attack of the carbonyl oxygen at the phosphonium atom of intermediate **A** affords the 1,2-oxaphospholene **5**. Subsequent C=C bond rearrangement would afford 1,2-oxaphospholene **7** (path B). When R^1 = aryl, the cycloaddition reaction of resonance form **B** with O_2 produces the five-membered cyclic oxyphosphorane **C**. Subsequent intramolecular [1,2]-phenyl group migration cleaving the O−O linkage affords zwitterion **D**.[13] In this step, triarylphosphine with electron-withdrawing groups on the aromatic ring may have a better migratory aptitude than electron-donating groups due to its stabilization effect on the positively charged phosphorus center in **D**, which was nucleophilically attacked by $H_2{}^{18}O$ at the phosphorus atom to give the intermediate **E**. Finally, the intermediate **E** eliminates the phenol to furnish the final product **3** (path A).

Diverse Transformations of Vinylcyclopropanol. The vinylcyclopropanol is a common motif in numerous natural products and valuable intermediates for further elaboration.[14] For example, the vinylcyclopropanol **3e** was converted to phosphoryl-substituted 5*H*-benzo[7]annulen-7(6*H*)-one **8** in 84% yield via intramolecular radical cyclization[15] (Scheme 7). The structure of **8** was unambiguously established by single-crystal X-ray diffraction analysis (Figure S2, Supporting Information). The functionalized (*Z*)-ene-1,4-dione **9** can be easily prepared in 80% yield with excellent stereoselectivity via the Au(I)-catalyzed rearrangement[16] of vinylcyclopropanol **3e**. Furthermore, a two-step strategy[4] was developed for the synthesis of the unsymmetrical divinyl ketone **10** in 82% yield (Scheme 8).

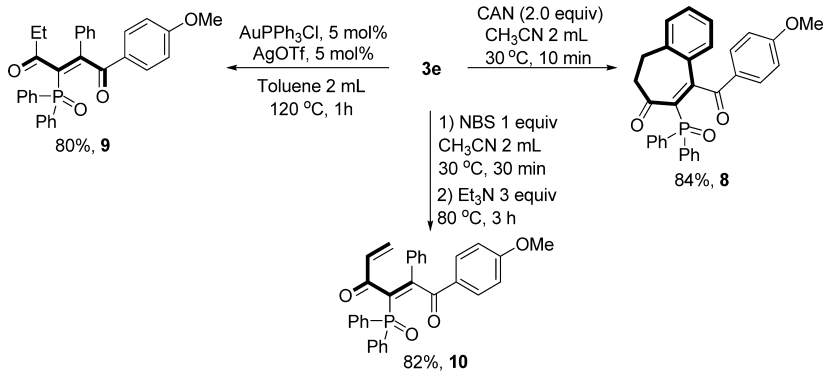
■ CONCLUSION

In conclusion, we have observed a unique carbon−phosphorus bond cleavage in the hydroxyphosphinylation reaction of 3-cyclopropylideneprop-2-en-1-ones with phosphines, which provides an efficient entry to highly functionalized 1-dialkylphosphinyl-3-oxo-(1*Z*)-alkenyl cyclopropanols with high stereoselectivity. The product can be easily transformed to 5*H*-benzo[7]annulen-7(6*H*)-one, (*Z*)-ene-1,4-dione, and unsymmetrical divinyl ketone. Due to the easy availability of starting materials and simple and convenient operation, this reaction facilitates an easy introduction of the phosphorus functionality to produce cyclopropanols. In addition, a plausible reaction mechanism was proposed on the basis of a mechanistic study. Further studies including the scope and synthetic utility of the method are underway.

■ EXPERIMENTAL PROCEDURES

General Methods. Melting points are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 400, 100, and 162 MHz, respectively. The chemical shifts of ^{31}P NMR was taken with reference

Scheme 8. Diverse Transformations of Vinylcyclopropanol 3e



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to 85% H_3PO_4 in D_2O and those of ^1H and ^{13}C with reference to TMS, the residual protonated DMSO, or $CHCl_3$ in the corresponding deuterated solvent. Chemical shifts are expressed in ppm, and J values are given in Hz. Organic solvents used were dried by standard methods when necessary. THF, toluene, and CH_3OH were distilled from sodium−benzophenone, and DCM and CH_3CN were distilled from CaH_2; unless otherwise specified, acetone containing 1.12 mmol (20 mg) of H_2O/5 mL was used. Commercially available reagents were used without further purification. Petroleum ether refers to the fraction with a boiling point in the range 60−90 °C. All reactions were monitored by TLC with GF 254 silica gel coated plates. Flash column chromatography was carried out using 300−400 mesh silica gel.

Procedure for Synthesis of 3a−x: Typical Procedure for (*Z*)-3-(Diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-2-phenyl-1-*p*-tolylprop-2-en-1-one (3a). To a stirred solution of **1a** (39 mg, 0.150 mmol) in acetone (5 mL with 20 mg of H_2O) was added 1.5 equiv of triphenylphosphine (**2a**) (59 mg) in open air at 0 °C. After it was stirred for 10 h (monitored by TLC), the resulting mixture was concentrated under reduced pressure. The residue was subjected to flash column chromatography (petroleum ether/ethyl acetate 2/1 v/v) to give the desired product **3a** (53 mg, 0.111 mmol, 74%) as a white solid: mp 186−187 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.73−7.82 (m, 4H), 7.57 (d, J = 6.8 Hz, 2H), 7.30−7.52 (m, 11H), 7.06 (d, J = 8.0 Hz, 2H), 5.29 (bs, 1H), 2.28 (s, 3H), 0.40−0.49 (m, 2H), 0−0.08 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.5 (d, $^3J_{C-P}$ = 6.2 Hz), 155.8 (d, $^2J_{C-P}$ = 11.3 Hz), 142.7, 135.4 (d, $^3J_{C-P}$ = 15.0 Hz), 134.8 (d, $^1J_{C-P}$ = 91.9 Hz), 133.1, 132.3 (d, $^1J_{C-P}$ = 100.9 Hz), 131.9 (d, $^2J_{C-P}$ = 9.2 Hz), 131.3 (d, $^4J_{C-P}$ = 2.3 Hz), 129.0, 128.4, 128.3, 128.0, 127.8, 127.5 (d, $^3J_{C-P}$ = 11.9 Hz), 52.8 (d, $^2J_{C-P}$ = 10.2 Hz), 20.6, 15.8 (d, $^3J_{C-P}$ = 5.3 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.32; IR (neat) 3268, 1653, 1598, 1437, 1260, 1177, 1115, 746, 724, 692 cm^{-1}; MS (70 eV, EI) m/z (%) 478 (M^+, 13.91), 201 (100); TOF HRMS (EI) calcd for $C_{31}H_{27}O_3P$ (M^+) 478.1698, found 478.1702.

The following compounds were prepared according to this procedure.

*(Z)-3-(Diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3b**).* The reaction of **1b** (37 mg, 0.150 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3b** (48 mg, 0.103 mmol, 69%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 185−186 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.71−7.82 (m, 4H), 7.54−7.64 (m, 4H), 7.31−7.52 (m, 10H), 7.27 (t, J = 7.6 Hz, 2H), 5.28 (s, 1H), 0.40−0.48 (m, 2H), 0.01−0.09 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C): δ 193.9 (d, $^3J_{C-P}$ = 6.3 Hz), 155.7 (d, $^2J_{C-P}$ = 10.9 Hz), 135.5, 135.2 (d, $^3J_{C-P}$ = 14.4 Hz), 135.0 (d, $^1J_{C-P}$ = 93.1 Hz), 132.24 (d, $^1J_{C-P}$ = 100.7 Hz), 132.19, 132.0 (d, $^2J_{C-P}$ = 9.2 Hz), 131.3 (d, $^4J_{C-P}$ = 2.5 Hz), 128.9, 128.5, 128.3, 127.9, 127.6 (d, $^3J_{C-P}$ = 12.5 Hz), 127.4, 52.8 (d, $^2J_{C-P}$ = 11.5 Hz), 15.8 (d, $^3J_{C-P}$ = 5.5 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.37; IR (neat) 3412, 1653, 1597, 1435, 1264, 1227, 1158, 1114, 722, 690 cm^{-1}; MS (70 eV, EI) m/z (%) 464 (M^+, 7.05), 201 (100); TOF HRMS (EI) calcd for $C_{30}H_{25}O_3P$ (M^+) 464.1541, found 464.1544.

*(Z)-3-(Diphenylphosphoryl)-1-(4-fluorophenyl)-3-(1-hydroxycyclopropyl)-2-phenylprop-2-en-1-one (**3c**).* The reaction of **1c** (40 mg, 0.152 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3c** (63 mg, 0.131 mmol, 87%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 184−185 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.72−7.83 (m, 4H), 7.63−7.76 (m, 2H), 7.58 (d, J = 7.2 Hz, 2H), 7.30−7.54 (m, 9H), 7.06 (t, J = 8.8 Hz, 2H), 5.32 (s, 1H), 0.40−0.49 (m, 2H), 0.01−0.10 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 192.5 (d, $^3J_{C-P}$ = 6.4 Hz), 164.3 (d, $^1J_{C-F}$ = 250.5 Hz), 155.3 (d, $^2J_{C-P}$ = 11.0 Hz), 135.3 (d, $^1J_{C-P}$ = 91.6 Hz), 135.0 (d, $^3J_{C-P}$ = 14.4 Hz), 132.3 (d, $^4J_{C-F}$ = 2.1 Hz), 132.2 (d, $^1J_{C-P}$ = 102.1 Hz), 132.0 (d, $^2J_{C-P}$ = 10.1 Hz), 131.7 (d, $^3J_{C-F}$ = 9.1 Hz), 131.4 (d, $^4J_{C-P}$ = 2.2 Hz), 128.6, 128.3, 128.0, 127.6 (d, $^3J_{C-P}$ = 12.5 Hz), 114.6 (d, $^2J_{C-F}$ = 22.0 Hz), 52.8 (d, $^2J_{C-P}$ = 10.5 Hz), 15.8 (d, $^3J_{C-P}$ = 5.6 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.40; IR (neat) 3373, 1662, 1595, 1438, 1263, 1228, 1157, 1118, 827, 727, 695 cm^{-1}; MS (70 eV, EI) m/z (%) 482 (M^+, 5.41), 201 (100); TOF HRMS (EI) calcd for $C_{30}H_{24}O_3PF$ (M^+): 482.1447, found 482.1445.

*(Z)-1-(4-Bromophenyl)-3-(diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-2-phenylprop-2-en-1-one (**3d**).* The reaction of **1d** (49 mg, 0.151 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3d** (74 mg, 0.136 mmol, 90%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 188−189 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.71−7.85 (m, 4H), 7.30−7.65 (m, 15H), 5.28 (s, 1H), 0.36−0.50 (m, 2H), −0.01 to 0.11 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.0 (d, $^3J_{C-P}$ = 5.9 Hz), 155.3 (d, $^2J_{C-P}$ = 10.5 Hz), 135.5 (d, $^1J_{C-P}$ = 91.2 Hz), 134.8 (d, $^3J_{C-P}$ = 17.1 Hz), 134.7, 132.2 (d, $^1J_{C-P}$ = 101.6 Hz), 131.9 (d, $^2J_{C-P}$ = 10.6 Hz), 131.4, 130.7, 130.6, 128.6, 128.3, 128.0, 127.8, 127.6 (d, $^3J_{C-P}$ = 12.7 Hz), 52.6 (d, $^2J_{C-P}$ = 11.8 Hz), 15.8 (d, $^3J_{C-P}$ = 5.1 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.13; IR (neat) 3260, 1659, 1580, 1486, 1257, 1235, 1181, 1115, 878, 745, 725, 693 cm^{-1}; MS (70 eV, EI) m/z (%) 542 ($M(^{79}Br)^+$, 4.32), 544 ($M(^{81}Br)^+$, 7.08), 201 (100); TOF HRMS (EI) calcd for $C_{30}H_{24}O_3P^{79}Br$ (M^+): 542.0646, found 542.0639.

*(Z)-3-(Diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-1-(4-methoxyphenyl)-2-phenylprop-2-en-1-one (**3e**).* The reaction of **1e** (41 mg, 0.149 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3e** (54 mg, 0.109 mmol, 73%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 205−206 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.71−7.82 (m, 4H), 7.57 (d, J = 7.6 Hz, 2H), 7.29−7.54 (m, 11H), 6.76 (d, J = 8.8 Hz, 2H), 5.35 (s, 1H), 3.77 (s, 3H), 0.40−0.50 (m, 2H), 0.01−0.06 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 192.4 (d, $^3J_{C-P}$ = 6.1 Hz), 162.6, 155.7 (d, $^2J_{C-P}$ = 10.9 Hz), 135.5 (d, $^3J_{C-P}$ = 14.8 Hz), 134.6 (d, $^1J_{C-P}$ = 92.9 Hz), 132.2 (d, $^1J_{C-P}$ = 100.5 Hz), 131.9 (d, $^2J_{C-P}$ = 10.3 Hz), 131.33 (d, $^4J_{C-P}$ = 2.9 Hz), 131.26, 128.6, 128.5, 128.2, 128.7, 127.5 (d, $^3J_{C-P}$ = 11.3 Hz), 112.9, 55.1, 53.1 (d, $^2J_{C-P}$ = 10.8 Hz), 15.8 (d, $^3J_{C-P}$ = 5.1 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.87; IR (neat) 3247, 1647, 1595, 1568, 1438, 1254, 1173, 1115, 1027, 832, 747, 694 cm^{-1}; MS (70 eV, EI) m/z (%) 494 (M^+, 6.98), 135 (100), 201 (92.61); TOF HRMS (EI) calcd for $C_{31}H_{27}O_4P$ (M^+) 494.1647, found 494.1639.

*(Z)-3-(Diphenylphosphoryl)-1-(furan-2-yl)-3-(1-hydroxycyclopropyl)-2-phenylprop-2-en-1-one (**3f**).* The reaction of **1f** (35 mg, 0.148 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3f** (38 mg, 0.084 mmol, 56%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 197−198 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.70−7.83 (m, 4H), 7.31−7.69 (m, 12H), 6.72 (s, 1H), 6.40 (s, 1H), 5.39 (s, 1H), 0.39−0.49 (m, 2H), −0.04 to 0.06 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 181.6 (d, $^3J_{C-P}$ = 6.3 Hz), 153.9 (d, $^2J_{C-P}$ = 11.7 Hz), 151.4, 146.7, 135.8 (d, $^1J_{C-P}$ = 91.9 Hz), 135.2 (d, $^3J_{C-P}$ = 14.4 Hz), 132.1 (d, $^1J_{C-P}$ = 100.9 Hz), 131.8 (d, $^2J_{C-P}$ = 10.0 Hz), 131.4 (d, $^4J_{C-P}$ = 2.4 Hz), 128.6, 128.4, 127.8, 127.5 (d, $^2J_{C-P}$ = 12.0 Hz), 118.9, 111.8, 53.2 (d, $^2J_{C-P}$ = 9.5 Hz), 15.8 (d, $^3J_{C-P}$ = 5.1 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 30.52; IR (neat) 3418, 1638, 1561, 1486, 1456, 1228, 1156, 1116, 773, 698 cm^{-1}; MS (70 eV, EI) m/z (%) 454 (M^+, 13.12), 201 (100); TOF HRMS (EI) calcd for $C_{28}H_{23}O_4P$ (M^+) 454.1334, found 454.1341.

*(Z)-3-(Diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-2-phenyl-1-(thien-2-yl)prop-2-en-1-one (**3g**).* The reaction of **1g** (38 mg, 0.151 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3g** (31 mg, 0.066 mmol, 43%) as white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 199−200 °C (petroleum ether/ethyl acetate); ^1H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.70−7.84 (m, 5H), 7.59 (d, J = 5.2 Hz, 2H), 7.34−7.54 (m, 9H), 7.25 (s, 1H), 6.92 (s, 1H), 5.42 (s, 1H), 0.40−0.50 (m, 2H), −0.04 to 0.08 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 186.4 (d, $^3J_{C-P}$ = 6.2 Hz), 154.5 (d, $^2J_{C-P}$ = 11.0 Hz), 142.9, 135.57 (d, $^3J_{C-P}$ = 14.8 Hz), 135.56 (d, $^1J_{C-P}$ = 90.5 Hz), 134.3, 134.2, 132.0 (d, $^1J_{C-P}$ = 101.3 Hz), 131.9 (d, $^2J_{C-P}$ = 9.7 Hz), 131.4, 128.7, 128.4, 127.9, 127.4 (d, $^3J_{C-P}$ = 12.0 Hz), 127.3, 53.2 (d, $^2J_{C-P}$ = 9.7 Hz), 15.9 (d, $^3J_{C-P}$ = 5.2 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 30.09; IR (neat) 3409, 1627, 1435, 1275, 1227, 1156, 1115, 835, 724, 693 cm^{-1}; MS (70 eV, EI) $m/$

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z (%) 470 (M^+, 5.50), 201 (100); TOF HRMS (EI) calcd for $C_{28}H_{23}O_3PS$ (M^+) 470.1106, found 470.1103.

*(Z)-1-(4-Chlorophenyl)-3-(diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-2-(2-methoxyphenyl)prop-2-en-1-one (**3h**).* The reaction of **1h** (47 mg, 0.152 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3h** (45 mg, 0.085 mmol, 57%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 167−168 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.75−7.85 (m, 4H), 7.66 (d, J = 7.2 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.38−7.49 (m, 6H), 7.33 (t, J = 8.4 Hz, 1H), 7.27 (d, J = 8.4 Hz, 2H), 7.02 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 8.0 Hz, 1H), 5.26 (s, 1H), 3.64 (s, 3H), 0.40−0.47 (m, 2H), 0.10−0.18 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 192.5 (d, $^3J_{C-P}$ = 5.6 Hz), 155.9, 151.4 (d, $^2J_{C-P}$ = 10.7 Hz), 139.0 (d, $^1J_{C-P}$ = 90.7 Hz), 136.9, 134.6, 132.3 (d, $^1J_{C-P}$ = 101.4 Hz), 132.0 (d, $^2J_{C-P}$ = 10.0 Hz), 131.2 (d, $^4J_{C-P}$ = 2.5 Hz), 130.9, 130.5, 130.2, 127.5 (d, $^3J_{C-P}$ = 12.4 Hz), 127.2, 124.9 (d, $^3J_{C-P}$ = 14.3 Hz), 120.3, 111.8, 55.4, 54.0 (d, $^2J_{C-P}$ = 10.1 Hz), 15.3 (d, $^3J_{C-P}$ = 5.7 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 32.66; IR (neat) 3316, 1670, 1587, 1482, 1435, 1256, 1230, 1149, 1116, 1094, 1004, 829, 766, 725, 693 cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 528 ($M(^{35}Cl)^+$, 7.99), 530 ($M(^{37}Cl)^+$, 3.80), 201 (100); TOF HRMS (EI) calcd for $C_{31}H_{26}O_4P^{35}Cl$ (M^+) 528.1257, found 528.1254.

*(Z)-3-(Diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-1-phenyl-2-m-tolylprop-2-en-1-one (**3i**).* The reaction of **1i** (39 mg, 0.150 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3i** (52 mg, 0.109 mmol, 72%) as white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 161−162 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.70−7.84 (m, 4H), 7.61 (d, J = 8.0 Hz, 2H), 7.33−7.51 (m, 9H), 7.21−7.31 (m, 3H), 7.15 (d, J = 7.6 Hz, 1H), 5.28 (s, 1H), 2.29 (s, 3H), 0.41−0.49 (m, 2H), 0.01−0.10 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.9 (d, $^3J_{C-P}$ = 5.9 Hz), 155.8 (d, $^2J_{C-P}$ = 10.6 Hz), 137.2, 135.5, 135.1 (d, $^3J_{C-P}$ = 14.8 Hz), 134.8 (d, $^1J_{C-P}$ = 92.2 Hz), 132.23 (d, $^1J_{C-P}$ = 100.5 Hz), 132.15, 131.9 (d, $^2J_{C-P}$ = 10.1 Hz), 131.3 (d, $^4J_{C-P}$ = 2.4 Hz), 129.2, 128.9, 128.6, 127.7, 127.5 (d, $^3J_{C-P}$ = 11.7 Hz), 127.4, 125.5, 52.8 (d, $^2J_{C-P}$ = 10.3 Hz), 20.5, 15.8 (d, $^3J_{C-P}$ = 5.5 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 32.66; IR (neat) 3365, 1662, 1595, 1439, 1262, 1228, 1157, 1117, 928, 729, 691 cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 478 (M^+, 4.89), 201 (100); TOF HRMS (EI) calcd for $C_{31}H_{27}O_3P$ (M^+) 478.1698, found 478.1704.

*(Z)-3-(Diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-2-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (**3j**).* The reaction of **1j** (41 mg, 0.149 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3j** (67 mg, 0.136 mmol, 90%) as white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 180−181 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.70−7.80 (m, 4H), 7.57 (d, J = 7.2 Hz, 2H), 7.35−7.54 (m, 9H), 7.2−7.30 (m, 2H), 6.93 (d, J = 8.0 Hz, 2H), 5.29 (s, 1H), 3.75 (s, 3H), 0.45−0.55 (m, 2H), 0.04−0.12 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 194.0 (d, $^3J_{C-P}$ = 6.2 Hz), 159.7, 155.4 (d, $^2J_{C-P}$ = 12.3 Hz), 135.6, 133.7 (d, $^1J_{C-P}$ = 93.0 Hz), 132.3 (d, $^1J_{C-P}$ = 100.3 Hz), 132.1, 131.9 (d, $^2J_{C-P}$ = 11.1 Hz), 131.3 (d, $^4J_{C-P}$ = 1.8 Hz), 130.0, 128.9, 127.5 (d, $^3J_{C-P}$ = 12.5 Hz), 127.4, 127.2 (d, $^3J_{C-P}$ = 15.3 Hz), 113.6, 54.8, 52.9 (d, $^2J_{C-P}$ = 11.4 Hz), 16.0 (d, $^3J_{C-P}$ = 5.4 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.64; IR (neat) 3432, 1661, 1596, 1510, 1438, 1256, 1226, 1159, 1118, 1024, 825, 741, 687 cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 494 (M^+, 6.14), 201 (100); TOF HRMS (EI) calcd for $C_{31}H_{27}O_4P$ (M^+) 494.1647, found 494.1650.

*(Z)-3-(Diphenylphosphoryl)-2-(4-fluorophenyl)-3-(1-hydroxycyclopropyl)-1-phenylprop-2-en-1-one (**3k**).* The reaction of **1k** (40 mg, 0.152 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3k** (68 mg, 0.141 mmol, 94%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 195−196 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.71−7.83 (m, 4H), 7.56−7.67 (m, 4H), 7.36−7.54 (m, 7H), 7.24−7.33 (m, 2H), 7.18 (t, J = 8.6 Hz, 2H), 5.30 (s, 1H), 0.40−0.55 (m, 2H), 0.02−0.13 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.8 (d, $^3J_{C-P}$ = 4.9 Hz), 162.1 (d, $^1J_{C-F}$ = 250.5 Hz), 154.8 (d, $^2J_{C-P}$ = 11.8 Hz), 135.43, 135.37 (d, $^1J_{C-P}$ = 91.6 Hz), 132.3, 132.18 (d, $^1J_{C-P}$ = 102.0 Hz), 131.9 (d, $^2J_{C-P}$ = 10.5 Hz), 131.5 (d, $^4J_{C-F}$ = 3.3 Hz), 131.4, 130.7 (d, $^3J_{C-F}$ = 8.1 Hz), 128.9, 127.6 (d, $^3J_{C-P}$ = 12.9 Hz), 127.5, 114.9(d, $^2J_{C-F}$ = 22.2 Hz), 52.7 (d, $^2J_{C-P}$ = 10.1 Hz), 15.8 (d, $^3J_{C-P}$ = 4.4 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.18; IR (neat) 3203, 1735, 1660, 1594, 1504, 1437, 1229, 1179, 1110, 732, 686 cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 482 (M^+, 4.30), 201 (100); TOF HRMS (EI) calcd for $C_{30}H_{24}O_3PF$ (M^+) 482.1447, found 482.1448.

*(Z)-3-(Diphenylphosphoryl)-3-(1-hydroxycyclopropyl)-2-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (**2l**).* The reaction of **1l** (44 mg, 0.149 mmol) and triphenylphosphine (**2a**; 59 mg, 1.5 equiv) at 0 °C afforded **3l** (61 mg, 0.119 mmol, 79%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 127−128 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 8.03 (s, 1H), 7.75−7.95 (m, 8H), 7.65 (d, J = 8.0 Hz, 2H), 7.33−7.55 (m, 9H), 7.25 (t, J = 7.2 Hz, 2H), 5.38 (s, 1H), 0.40−0.47 (m, 2H), 0.03−0.10 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.8 (d, $^3J_{C-P}$ = 5.6 Hz), 155.7 (d, $^2J_{C-P}$ = 10.9 Hz), 135.5, 135.4 (d, $^1J_{C-P}$ = 91.3 Hz), 132.7 (d, $^3J_{C-P}$ = 14.8 Hz), 132.4, 132.20, 132.18 (d, $^1J_{C-P}$ = 100.5 Hz), 132.1, 132.0 (d, $^2J_{C-P}$ = 10.5 Hz), 131.4 (d, $^4J_{C-P}$ = 2.0 Hz), 128.9, 128.0, 127.6 (d, $^3J_{C-P}$ = 12.5 Hz), 127.4, 127.1, 126.6, 126.2, 126.1, 52.9 (d, $^2J_{C-P}$ = 11.0 Hz), 15.8 (d, $^3J_{C-P}$ = 5.5 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.48; IR (neat) 3299, 1658, 1591, 1437, 1245, 1172, 1117, 1100, 1001, 731, 684 cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 514 (M^+, 3.97), 201 (100); TOF HRMS (EI) calcd for $C_{34}H_{27}O_3P$ (M^+) 514.1698, found 514.1695.

*(Z)-3-(Bis(4-methoxyphenyl)phosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3m**).* The reaction of **1b** (37 mg, 0.150 mmol) and tris(4-methoxyphenyl)phosphine (**2b**; 79 mg, 1.5 equiv) at 0 °C afforded **3m** (63 mg, 0.120 mmol, 80%) as a white solid (eluent: petroleum ether/ethyl acetate 1/1): mp 194−195 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.58−7.70 (m, 4H), 7.50−7.57 (m, 4H), 7.30−7.44 (m, 4H), 7.25 (t, J = 7.4 Hz, 2H), 6.92 (d, J = 6.8 Hz, 4H), 5.41 (s, 1H), 3.77 (s, 6H), 0.45−0.51 (m, 2H), −0.02 to 0.06 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 194.1 (d, $^3J_{C-P}$ = 6.0 Hz), 161.8 (d, $^4J_{C-P}$ = 2.8 Hz), 154.4 (d, $^2J_{C-P}$ = 10.8 Hz), 136.1 (d, $^1J_{C-P}$ = 92.7 Hz), 135.2 (d, $^3J_{C-P}$ = 14.9 Hz), 135.0, 133.9 (d, $^2J_{C-P}$ = 10.9 Hz), 132.2, 129.0, 128.5, 128.3, 127.9, 127.3, 123.1 (d, $^1J_{C-P}$ = 107.2 Hz), 113.4 (d, $^3J_{C-P}$ = 12.7 Hz), 54.9, 53.3 (d, $^2J_{C-P}$ = 10.3 Hz), 15.5 (d, $^3J_{C-P}$ = 5.5 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.85; IR (neat) 3276, 1655, 1595, 1569, 1501, 1294, 1256, 1096, 1022, 825, 800, 704, 672 cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 524 (M^+, 4.18), 261 (100); TOF HRMS (EI) calcd for $C_{32}H_{29}O_5P$ (M^+) 524.1753, found 524.1757.

*(Z)-3-(Bis(3,5-dimethoxyphenyl)phosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3n**).* The reaction of **1b** (37 mg, 0.15 mmol) and tris(3,5-dimethoxyphenyl)phosphine (**2c**; 99 mg, 1.5 equiv) at 0 °C afforded 3,5-dimethoxyphenol (18 mg, 0.117 mmol, 78%) as an yellow oil (eluent: petroleum ether/ethyl acetate 6/1) and **3n** (68 mg, 0.116 mmol, 78%) as a white solid (eluent: petroleum ether/ethyl acetate 1/2): mp 157−158 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.50−7.65 (m, 4H), 7.18−7.45 (m, 6H), 6.85−7.02 (m, 4H), 6.54 (s, 2H), 5.45 (s, 1H), 3.75 (s, 12H), 0.40−0.60 (m, 2H), −0.03 to 0.16 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.8 (d, $^3J_{C-P}$ = 4.9 Hz), 159.9 (d, $^3J_{C-P}$ = 17.7 Hz), 155.3 (d, $^2J_{C-P}$ = 12.1 Hz), 135.2 (d, $^3J_{C-P}$ = 15.2 Hz), 134.9, 134.8 (d, $^1J_{C-P}$ = 92.9 Hz), 133.5 (d, $^1J_{C-P}$ = 99.9 Hz), 132.3, 128.8, 128.6, 128.3, 127.9, 127.3, 110.2 (d, $^2J_{C-P}$ = 11.5 Hz), 103.6, 55.1, 53.1 (d, $^2J_{C-P}$ = 10.8 Hz), 15.7 (d, $^3J_{C-P}$ = 5.3 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.65; IR (neat) 1652, 1589, 1451, 1418, 1290, 1205, 1158, 1064, 874, 708, 629 cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 584 (M^+, 6.49), 321 (100); TOF HRMS (EI) calcd for $C_{34}H_{33}O_7P$ (M^+) 584.1964, found 584.1962.

3,5-Dimethoxyphenol:[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06−6.09 (m, 1H), 6.03 (d, J = 2.4 Hz, 2H), 5.51 (s, 1H), 3.74 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 157.4, 94.3, 93.1, 55.3; IR (neat) 3387, 1597, 1550, 1459, 1342, 1195, 1143, 1057, 820, 680 cm^{-1}; MS (70 eV, EI) *m*/*z* (%) 154 (M^+, 100), 125 (81.22).

*(Z)-3-(Bis(4-fluorophenyl)phosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3o**).* The reaction of **1b** (37 mg, 0.150 mmol) and tris(4-fluorophenyl)phosphine (**2d**; 71 mg, 1.5 equiv) at 0 °C and then room temperature for 10 h afforded **3o** (38 mg, 0.076

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mmol, 50%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 200−201 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.72−7.89 (m, 4H), 7.51−7.65 (m, 4H), 7.10−7.50 (m, 10H), 5.39 (s, 1H), 0.40−0.52 (m, 2H), −0.02 to 0.13 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 194.0 (d, $^3J_{C-P}$ = 5.7 Hz), 164.0 (dd, $^4J_{C-P}$ = 2.6 Hz, $^1J_{C-F}$ = 249.8 Hz,), 155.9 (d, $^2J_{C-P}$ = 11.6 Hz), 135.3, 135.1, 134.8 (d, $^1J_{C-P}$ = 89.7 Hz), 114.9 (dd, $^2J_{C-P}$ = 11.6 Hz, $^3J_{C-F}$ = 8.7 Hz), 132.4, 128.9, 128.7, 127.9, 127.5, 134.9 (dd, $^3J_{C-P}$ = 13.5 Hz, $^2J_{C-F}$ = 21.3 Hz), 52.8 (d, $^2J_{C-P}$ = 11.9 Hz), 15.9 (d, $^3J_{C-P}$ = 5.2 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 24.31; IR (neat) 3412, 1656, 1579, 1482, 1389, 1259, 1227, 1160, 1087, 821, 755, 705 cm^{-1}; MS (70 eV, EI) m/z (%) 500 (M$^+$, 4.70), 237 (100); TOF HRMS (EI) calcd for $C_{30}H_{23}O_3F_2P$ (M$^+$) 500.1353, found 500.1354.

*(Z)-3-(Bis(4-chlorophenyl)phosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3p**).* The reaction of **1b** (37 mg, 0.150 mmol) abs tris(4-chlorophenyl)phosphine (**2e**; 82 mg, 1.5 equiv) at 0 °C 10 h and then room temperature for 10 h afforded **3p** (38 mg, 0.071 mmol, 48%) as a white solid (eluent: chloroform/ethyl acetate 8/1): mp 185−186 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.68−7.81 (m, 4H), 7.53−7.64 (m, 4H), 7.42−7.51 (m, 5H), 7.34−7.41 (m, 5H), 5.40 (s, 1H), 0.42−0.50 (m, 2H), 0.04−0.12 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.9 (d, $^3J_{C-P}$ = 6.1 Hz), 156.3 (d, $^2J_{C-P}$ = 11.5 Hz), 137.0 (d, $^4J_{C-P}$ = 2.5 Hz), 135.2, 134.9 (d, $^3J_{C-P}$ = 15.7 Hz), 134.5 (d, $^1J_{C-P}$ = 92.3 Hz), 133.8 (d, $^2J_{C-P}$ = 11.8 Hz), 132.4, 130.9 (d, $^1J_{C-P}$ = 102.9 Hz), 128.9, 128.7, 128.3, 128.0, 127.9 (d, $^3J_{C-P}$ = 13.0 Hz), 127.5, 52.7 (d, $^2J_{C-P}$ = 10.1 Hz), 15.9 (d, $^3J_{C-P}$ = 5.6 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.67; IR (neat) 3412, 1656, 1579, 1482, 1389, 1259, 1227, 1160, 1087, 821, 755, 705 cm^{-1}; MS (70 eV, EI) m/z (%) 532 (M(^{35,35}Cl) +, 3.34), 534 (M(^{35,37}Cl) $^+$, 2.53), 536 (M(^{37,37}Cl)$^+$, 0.79), 105 (100); TOF HRMS (EI) calcd for $C_{30}H_{23}O_3P^{35}Cl_2$ (M$^+$) 532.0762, found 532.0765.

*(Z)-3-(Di-p-tolylphosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3q**).* The reaction of **1b** (37 mg, 0.150 mmol) and tris(4-methylphenyl)phosphine (**2f**; 68 mg, 1.5 equiv) at 0 °C afforded **3q** (47 mg, 0.096 mmol, 64%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 181−182 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.47−7.70 (m, 8H), 7.29−7.45 (m, 4H), 7.10−7.29 (m, 6H), 5.35 (s, 1H), 2.28 (s, 6H), 0.40−0.54 (m, 2H), −0.03 to 0.10 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.9 (d, $^3J_{C-P}$ = 6.1 Hz), 154.9 (d, $^2J_{C-P}$ = 10.9 Hz), 141.5 (d, $^4J_{C-P}$ = 1.9 Hz), 135.7 (d, $^1J_{C-P}$ = 92.0 Hz), 135.2 (d, $^3J_{C-P}$ = 14.2 Hz), 135.0, 132.1, 132.0 (d, $^2J_{C-P}$ = 11.3 Hz), 128.9, 128.8 (d, $^1J_{C-P}$ = 102.2 Hz), 128.5, 128.3, 128.2 (d, $^3J_{C-P}$ = 13.1 Hz), 127.9, 127.2, 53.1 (d, $^2J_{C-P}$ = 10.3 Hz), 20.5, 15.6 (d, $^3J_{C-P}$ = 5.4 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 30.11; IR (neat) 3354, 1658, 1599, 1446, 1392, 1259, 1232, 1148, 1118, 1097, 808, 707, 662 cm^{-1}; MS (70 eV, EI) m/z (%) 492 (M$^+$, 3.92), 229 (100); TOF HRMS (EI) calcd for $C_{32}H_{29}O_3P$ (M$^+$) 492.1854, found 492.1855.

*(Z)-3-(Dim-tolylphosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3r**).* The reaction of **1b** (37 mg, 0.15o mmol), tris(3-methylphenyl)phosphine (**2g**; 68 mg, 1.5 equiv) at 0 °C afforded **3r** (51 mg, 0.104 mmol, 69%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 155−156 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.45−7.65 (m, 8H), 7.15−7.44 (m, 10H), 5.40 (s, 1H), 2.27 (s, 6H), 0.40−0.55 (m, 2H), −0.04 to 0.10 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.8 (d, $^3J_{C-P}$ = 5.8 Hz), 155.1 (d, $^2J_{C-P}$ = 11.3 Hz), 137.0 (d, $^3J_{C-P}$ = 11.3 Hz), 135.4 (d, $^1J_{C-P}$ = 91.6 Hz), 135.21 (d, $^3J_{C-P}$ = 12.5 Hz), 135.15, 132.3 (d, $^2J_{C-P}$ = 10.3 Hz), 132.1 (d, $^3J_{C-P}$ = 15.4 Hz), 132.0, 131.9 (d, $^1J_{C-P}$ = 100.8 Hz), 129.2 (d, $^2J_{C-P}$ = 10.7 Hz), 128.8, 128.5, 128.3, 127.9, 127.4 (d, $^3J_{C-P}$ = 12.8 Hz), 127.3, 53.1 (d, $^2J_{C-P}$ = 10.8 Hz), 20.5, 15.8 (d, $^3J_{C-P}$ = 4.8 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 30.28; IR (neat) 3368, 1662, 1595, 1448, 1392, 1259, 1227, 1150, 1114, 872, 707, 653 cm^{-1}; MS (70 eV, EI) m/z (%) 492 (M$^+$, 4.45), 229 (100); TOF HRMS (EI) calcd for $C_{32}H_{29}O_3P$ (M$^+$) 492.1854, found 492.1850.

*(Z)-3-(Dinaphthalen-2-ylphosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2- en-1-one (**3s**).* The reaction of **1b** (37 mg, 0.150 mmol) and tris(2-naphthylphenyl)phosphine (**2j**; 93 mg, 1.5 equiv) at 0 °C afforded **3s** (63 mg, 0.112 mmol, 74%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 175−176 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 8.41 (d, J = 12.8 Hz, 2H), 7.80−8.02 (m, 8H), 7.41−7.71 (m, 8H), 7.30−7.46 (m, 3H), 7.16 (s, 1H), 7.04 (s, 2H), 5.48 (s, 1H), 0.40−0.59 (m, 2H), 0.05−0.21 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 194.0 (d, $^3J_{C-P}$ = 5.6 Hz), 155.8 (d, $^2J_{C-P}$ = 11.9 Hz), 135.221 (d, $^3J_{C-P}$ = 14.2 Hz), 135.217 (d, $^1J_{C-P}$ = 93.0 Hz), (135.0, 134.0, 133.9, overlap), 133.9, 132.0, 131.5 (d, $^2J_{C-P}$ = 12.6 Hz), 129.6 (d, $^1J_{C-P}$ = 100.2 Hz), 128.6, 128.4 (d, $^3J_{C-P}$ = 15.8 Hz), 127.9 (d, $^3J_{C-P}$ = 14.1 Hz), (127.2, 127.2, 127.1, 127.1, overlap), 126.3, 53.1 (d, $^2J_{C-P}$ = 11.2 Hz), 15.9 (d, $^3J_{C-P}$ = 4.6 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.83; IR (neat) 3056, 1658, 1592, 1448, 1260, 1227, 1155, 1088, 858, 819, 747, 705, 659 cm^{-1}; MS (70 eV, EI) m/z (%) 564 (M$^+$, 12.66), 301 (100); TOF HRMS (EI) calcd for $C_{38}H_{29}O_3P$ (M$^+$) 564.1854, found 564.1857.

*(Z)-3-(Butyl(phenyl)phosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3t**).* The reaction of **1b** (37 mg, 0.150 mmol) and *n*-butyldiphenylphosphine (**2k**; 54 mg, 1.5 equiv) at 0 °C afforded **3t** (49 mg, 0.110 mmol, 73%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 85−86 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.70−7.90 (m, 4H), 7.20−7.60 (m, 11H), 5.49 (s, 1H), 2.25−2.47 (m, 2H), 1.65 (m, 1H), 1.30−1.54 (m, 3H), 0.75−1.00 (m, 3H), 0.35−0.60 (m, 2H), −0.10 to 0.10 (m, 1H), −0.30 to −0.16 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 194.0 (d, $^3J_{C-P}$ = 5.7 Hz), 155.1 (d, $^2J_{C-P}$ = 9.0 Hz), 136.6, 135.5 (d, $^3J_{C-P}$ = 14.3 Hz), 135.4 (d, $^1J_{C-P}$ = 83.7 Hz), 134.3 (d, $^1J_{C-P}$ = 92.8 Hz), 131.8, 130.84, 130.8 (d, $^2J_{C-P}$ = 8.8 Hz), 128.6, 128.3, 128.2, 127.8, 127.7 (d, $^3J_{C-P}$ = 11.3 Hz), 127.6, 51.8 (d, $^2J_{C-P}$ = 10.8 Hz), 27.8 (d, $^1J_{C-P}$ = 69.2 Hz), 22.9 (d, $^2J_{C-P}$ = 15.8 Hz), 22.8 (d, $^3J_{C-P}$ = 4.4 Hz), 15.9 (d, $^3J_{C-P}$ = 7.5 Hz), 15.8 (d, $^3J_{C-P}$ = 2.8 Hz), 13.0; ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 33.57; IR (neat) 3210, 1666, 1594, 1489, 1255, 1224, 1153, 1110, 876, 747, 695, 648 cm^{-1}; MS (70 eV, EI) m/z (%) 444 (M$^+$, 3.51), 181 (36.81), 105 (100); TOF HRMS (EI) calcd for $C_{28}H_{29}O_3P$ (M$^+$) 444.1854, found 444.1843.

*(Z)-3-(Ethyl(phenyl)phosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3u**).* The reaction of **1b** (37 mg, 0.150 mmol) and ethyldiphenylphosphine (**2l**; 48 mg, 1.5 equiv) at 0 °C afforded **3u** (51 mg, 0.123 mmol, 82%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 175−176 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.70−7.90 (m, 4H), 7.20−7.60 (m, 11H), 5.51 (s, 1H), 2.25−2.47 (m, 2H), 1.00−1.23 (m, 3H), 0.30−0.60 (m, 2H), −0.10 to 0.10 (m, 1H), −0.30 to −0.17 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 194.1 (d, $^3J_{C-P}$ = 4.9 Hz), 155.5 (d, $^2J_{C-P}$ = 10.5 Hz), 136.6, 135.5 (d, $^3J_{C-P}$ = 12.3 Hz), 135.1 (d, $^1J_{C-P}$ = 83.6 Hz), 134.0 (d, $^1J_{C-P}$ = 94.3 Hz), 131.7, 130.86, 130.81 (d, $^2J_{C-P}$ = 9.4 Hz), 128.6, 128.3, 128.2, 127.8, 127.7 (d, $^3J_{C-P}$ = 8.9 Hz), 127.6, 51.7 (d, $^2J_{C-P}$ = 11.9 Hz), 20.9 (d, $^1J_{C-P}$ = 70.7 Hz), 15.9 (d, $^3J_{C-P}$ = 6.2 Hz), 15.7, 4.8 (d, $^2J_{C-P}$ = 3.8 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 34.88; IR (neat) 3158, 1665, 1595, 1444, 1254, 1225, 1148, 1108, 1028, 877, 727, 693, 646 cm^{-1}; MS (70 eV, EI) m/z (%) 416 (M$^+$, 8.67), 153 (65.84), 105 (100); TOF HRMS (EI) calcd for $C_{26}H_{25}O_3P$ (M$^+$) 416.1541, found 416.1548.

*(Z)-3-(Cyclopropyl(phenyl)phosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3v**).* The reaction of **1b** (37 mg, 0.150 mmol) and cyclopropyldiphenylphosphine (**2m**; 51 mg, 1.5 equiv) at 0 °C afforded **3v** (45 mg, 0.105 mmol, 70%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1): mp 162−163 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.73−7.96 (m, 4H), 7.20−7.65 (m, 11H), 5.46 (bs, 1H), 1.69−1.87 (m, 1H), 0.75−0.95 (m, 3H), 0.60−0.74 (m, 1H), 0.45−0.57 (m, 2H), 0.04−0.14 (m, 1H), −0.20-−0.03 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 194.3 (d, $^3J_{C-P}$ = 6.0 Hz), 154.3 (d, $^2J_{C-P}$ = 11.2 Hz), 136.3, 135.6 (d, $^1J_{C-P}$ = 90.4 Hz), 135.2 (d, $^3J_{C-P}$ = 13.8 Hz), 134.0 (d, $^1J_{C-P}$ = 98.7 Hz), 131.9, 130.8, 130.6 (d, $^2J_{C-P}$ = 10.1 Hz), 128.7, 128.31, 128.26, 127.8, 127.7 (d, $^3J_{C-P}$ = 8.9 Hz), 127.6, 51.7 (d, $^2J_{C-P}$ = 12.6 Hz), 16.1 (d, $^3J_{C-P}$ = 6.0 Hz), 15.3 (d, $^3J_{C-P}$ = 4.0 Hz), 5.9

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(d, $^1J_{C-P}$ = 101.8 Hz), 2.5 (d, $^2J_{C-P}$ = 4.4 Hz), 2.4 (d, $^2J_{C-P}$ = 2.3 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 32.46; IR (neat) 3276, 1669, 1443, 1254, 1253, 1152, 1109, 1027, 897, 724, 692 cm^{-1}; MS (70 eV, EI) m/z (%) 428 (M^+, 7.84), 323 (100), 165 (65.47); TOF HRMS (EI) calcd for $C_{27}H_{25}O_3P$ (M^+) 428.1541, found 428.1536.

*(Z)-3-((4-Chlorophenyl)(phenyl)phosphoryl)-3-(1-hydroxycyclopropyl)-1,2-diphenylprop-2-en-1-one (**3w**).* The reaction of **1b** (37 mg, 0.150 mmol) and bis(4-chlorophenyl)phenylphosphine (**2n**; 74 mg, 1.5 equiv) at 0 °C and then room temperature for 10 h afforded **3w** (42 mg, 0.084 mmol, 56%) as s white solid and **3o** (13 mg, 0.024 mmol, 16%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1). **3w**: mp 193−194 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.65−7.88 (m, 4H), 7.20−7.65 (m, 15H), 5.34 (s, 1H), 0.35−0.55 (m, 2H), −0.01−0.14 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.9 (d, $^3J_{C-P}$ = 4.5 Hz), 156.0 (d, $^2J_{C-P}$ = 11.2 Hz), 136.8 (d, $^4J_{C-P}$ = 2.0 Hz), 153.3, 135.0 (d, $^2J_{C-P}$ = 14.1 Hz), 134.7 (d, $^1J_{C-P}$ = 93.4 Hz), 133.9 (d, $^3J_{C-P}$ = 10.6 Hz), 132.3, 132.0 (d, $^1J_{C-P}$ = 100.3 Hz), 131.8 (d, $^3J_{C-P}$ = 10.4 Hz), 131.5, 131.1 (d, $^1J_{C-P}$ = 101.1 Hz), 128.9, 128.6, 128.3, 127.9, 127.7 (d, $^2J_{C-P}$ = 12.4 Hz), 127.5, 52.7 (d, $^2J_{C-P}$ = 10.2 Hz), 15.9 (d, $^3J_{C-P}$ = 4.7 Hz), 15.8 (d, $^3J_{C-P}$ = 5.2 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 28.74; IR (neat) 3400, 1654, 1579, 1481, 1385, 1261, 1226, 1158, 1116, 1091, 823, 746, 711 cm^{-1}; MS (70 eV, EI) m/z (%) 498 (M(^{35}Cl)$^+$, 6.66), 500(M(^{37}Cl)$^+$, 3.09), 235 (100); TOF HRMS (EI) calcd for $C_{30}H_{24}O_3P^{35}Cl$ (M^+) 498.1152, found 498.1159.

*(Z)-3-(1-hydroxycyclopropyl)-3-((4-methoxyphenyl)(phenyl)-phosphoryl)-1,2-diphenylprop-2-en-1-one (**3x**).* The reaction of **1b** (37 mg, 0.150 mmol) and bis(4-methoxyphenyl)phenylphosphine (**2o**; 66 mg, 1.5 equiv) at 0 °C afforded **3x** (56 mg, 0.113 mmol, 75%) and **3b** (3 mg, 0.06 mmol, 5%) as a white solid (eluent: petroleum ether/ethyl acetate 2/1). **3x**: mp 187−188 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.75−7.86 (m, 2H), 7.53−7.65 (m, 6H), 7.30−7.52 (m, 7H), 7.26 (t, J = 7.6 Hz, 2H), 6.89 (d, J = 7.6 Hz, 2H), 5.34 (s, 1H), 3.76 (s, 3H), 0.40−0.52 (m, 2H), −0.03−0.10 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 194.0 (d, $^3J_{C-P}$ = 5.8 Hz), 161.8, 155.0 (d, $^2J_{C-P}$ = 11.4 Hz), 135.6 (d, $^1J_{C-P}$ = 92.9 Hz), 135.21, 135.17 (d, $^3J_{C-P}$ = 13.7 Hz), 134.0 (d, $^2J_{C-P}$ = 11.1 Hz), 132.5 (d, $^1J_{C-P}$ = 100.7 Hz), 132.2, 131.8 (d, $^3J_{C-P}$ = 9.8 Hz), 131.3, 128.9, 128.5, 128.3, 127.9, 127.6 (d, $^2J_{C-P}$ = 12.6 Hz), 127.3, 122.8 (d, $^1J_{C-P}$ = 106.5 Hz), 113.3 (d, $^3J_{C-P}$ = 13.8 Hz), 54.9, 53.1 (d, $^2J_{C-P}$ = 11.0 Hz), 15.8 (d, $^3J_{C-P}$ = 5.0 Hz), 15.5 (d, $^3J_{C-P}$ = 5.5 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.62; IR (neat) 3393, 1655, 1596, 1572, 1500, 1295, 1258, 1220, 1157, 1116, 1019, 838, 705, 650 cm^{-1}; MS (70 eV, EI) m/z (%) 494 (M^+, 1.11), 232 (100); TOF HRMS (EI) calcd for $C_{31}H_{27}O_4P$ (M^+) 494.1647, found 494.1642.

Mechanistic Studies. ***7m***. To a stirred solution of **1m** (34 mg, 0.15 mmol) in acetone (5 mL with 20 mg of H_2O) was added 1.5 equiv of triphenylphosphine (**2a**; 59 mg, 1.5 equiv) in an air atmosphere at 0 °C. After it was stirred for 10 h, the resulting mixture was concentrated under reduced pressure. The residue was recrystallized (petroleum ether/dichloromethane 15/1) to give the product **7m** (56 mg, 0.115 mmol, 76%) as a white solid: mp 173−174 °C (petroleum ether/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.44 (m, 11H), 7.20−7.30 (m, 9H), 4.18 (d, J = 8.8 Hz, 1H), 2.34−2.46 (m, 1H), 0.67 (d, J = 6.4 Hz, 6H), 0.48−0.59 (m, 1H), −0.2−0.05 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (d, $^2J_{C-P}$ = 22.9 Hz), 151.5 (d, $^4J_{C-P}$ = 3.1 Hz), 143.8 (d, $^1J_{C-P}$ = 102.9 Hz), 136.7 (d, $^2J_{C-P}$ = 21.0 Hz), 131.7 (d, $^3J_{C-P}$ = 8.1 Hz), 130.0, 128.0, 127.6, 127.5, 126.9 (d, $^2J_{C-P}$ = 12.4 Hz), 126.6 (d, $^1J_{C-P}$ = 121.9 Hz), 111.5, 25.3, 23.2, 14.8 (d, $^2J_{C-P}$ = 20.6 Hz), 10.9 (d, $^3J_{C-P}$ = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C) δ −46.50; IR (neat) 2955, 1610, 1572, 1432, 1383, 1217, 1189, 1079, 1058, 805, 724, 692 cm^{-1}; MS (70 eV, EI) m/z (%) 488 (M^+, 11.8), 262 (100); TOF HRMS (EI) calcd for $C_{34}H_{33}OP$ (M^+) 488.2269, found 488.2262.

Selected bond lengths (Å) and angles (deg) for **7m**: P(1)−C(6) = 1.8213(18), P(1)−C(7) = 1.9046(17), P(1)−C(18) = 1.8319(19), P(1)−C(19) = 1.8393(18), P(1)−O(1) = 1.8578(12), O(1)−C(30) = 1.336(2); C(6)−P(1)−C(7) = 95.49(8), C(6)−P(1)−C(18) = 121.55(9), C(6)−P(1)−C(19) = 116.66(8), C(6)−P(1)−O(1) = 84.77(7), C(7)−P(1)−C(18) = 91.82(8), C(7)−P(1)−C(19) = 96.77(8), C(7)−P(1)−O(1) = 176.80(7), C(18)−P(1)−C(19) = 119.84(9), C(18)−P(1)−O(1) = 85.34(7), C(19)−P(1)−O(1) = 85.94(7), C(30)−O(1)−P(1) = 114.82(10).

3a-^{18}O. In an atmosphere of dry air, H_2O (27 mg, 1.5 mmol, 10 equiv) was added to a solution of **1a** (39 mg, 0.150 mmol) in 5 mL of dry DCM at room temperature. Then PPh_3 (79 mg, 0.3 mmol, 2 equiv) was added to the mixture. After it was stirred for 10 h (monitored by TLC), the reaction was followed by GC-MS. Filtration, evaporation, and flash chromatography on silica gel (petroleum ether/ethyl acetate 2/1 v/v) afforded **3a-^{18}O** (51 mg, 0.106 mmol, 71%) as a white solid: ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.73−7.82 (m, 4H), 7.57 (d, J = 6.8 Hz, 2H), 7.30−7.52 (m, 11H), 7.06 (d, J = 8.0 Hz, 2H), 5.30 (bs, 1H), 2.28 (s, 3H), 0.40−0.53 (m, 2H), −0.50 to 0.11 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 193.5 (d, $^3J_{C-P}$ = 5.0 Hz), 155.8 (d, $^2J_{C-P}$ = 11.3 Hz), 142.7, 135.4 (d, $^3J_{C-P}$ = 14.9 Hz), 134.7 (d, $^1J_{C-P}$ = 92.6 Hz), 133.1, 132.3 (d, $^1J_{C-P}$ = 100.5 Hz), 131.9 (d, $^2J_{C-P}$ = 9.7 Hz), 131.3 (d, $^4J_{C-P}$ = 3.0 Hz), 129.0, 128.4, 128.3, 128.0, 127.8, 127.5 (d, $^3J_{C-P}$ = 12.4 Hz), 52.9 (d, $^2J_{C-P}$ = 11.0 Hz), 20.6, 15.8 (d, $^3J_{C-P}$ = 7.6 Hz); ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 29.86.

Synthetic Applications. *8-(Diphenylphosphoryl)-9-(4-methoxybenzoyl)-5H-benzo[7]annulen-7(6H)-one (**8**).* To a stirred solution of **3e** (49 mg, 0.10 mmol) in CH_3CN (2 mL) was added 2.0 equiv of CAN (110 mg) at 30 °C. After it was stirred for 10 min (monitored by TLC), the resulting mixture was concentrated under reduced pressure. The residue was subjected to flash column chromatography (petroleum ether/ethyl acetate 4/1 v/v) to give the product **8** (41 mg, 0.083 mmol, 84%) as a white solid: mp 222−224 °C (petroleum ether/chloroform); ^{1}H NMR (400 MHz, DMSO-d_6, 80 °C) δ 7.69−7.80 (m, 4H), 7.66 (d, J = 8.4 Hz, 2H), 7.56−7.63 (m, 2H), 7.48−7.56 (m, 4H), 7.44 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.2 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 3.23 (m, 2H), 2.59 (t, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6, 80 °C) δ 203.4 (d, $^2J_{C-P}$ = 8.1 Hz), 192.1 (d, $^3J_{C-P}$ = 6.4 Hz), 162.9, 155.7 (d, $^4J_{C-P}$ = 3.5 Hz), 139.3, 137.7 (d, $^1J_{C-P}$ = 83.4 Hz), 133.2 (d, $^2J_{C-P}$ = 13.4 Hz), 131.9 (d, $^1J_{C-P}$ = 105.3 Hz), 131.6 (d, $^4J_{C-P}$ = 1.8 Hz), 131.5 (d, $^2J_{C-P}$ = 10.3 Hz), 130.8, 130.0, 129.5, 128.9, 127.9 (d, $^3J_{C-P}$ = 12.6 Hz), 127.3, 127.2, 113.5, 55.2, 49.7, 28.4; ^{31}P NMR (162 MHz, DMSO-d_6, 25 °C) δ 25.1; IR (neat) 3058, 1682, 1598, 1575, 1510, 1438, 1316, 1261, 1238, 1188, 1166, 1117, 1025, 973 cm^{-1}; MS (70 eV, EI) m/z (%) 492 (M^+, 12.53), 135 (100). TOF HRMS (EI) calcd for $C_{31}H_{25}O_4P$ (M^+) 492.1490, found 492.1495.

*(Z)-3-(Diphenylphosphoryl)-1-(4-methoxyphenyl)-2-phenylhex-2-ene-1,4-dione (**9**).* To a stirred solution of **3e** (49 mg, 0.10 mmol) in toluene (2 mL) was added 5% of $AuPPh_3Cl$ (2 mg) and AgOTf (1 mg) at 120 °C. After it was stirred for 1 h (monitored by TLC), the resulting mixture was concentrated under reduced pressure. The residue was subjected to flash column chromatography (petroleum ether/ethyl acetate 4/1 v/v) to give the product **9** (39 mg, 0.079 mmol, 80%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.78−7.87 (m, 4H), 7.72 (d, J = 8.4 Hz, 2H), 7.45−7.55 (m, 4H), 7.37−7.44 (m, 4H), 7.31−7.36 (m, 3H), 6.63 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 1.79 (q, J = 6.8 Hz, 2H), 0.45 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 206.8 (d, $^2J_{C-P}$ = 8.9 Hz), 192.2 (d, $^3J_{C-P}$ = 6.1 Hz), 163.4, 156.3 (d, $^4J_{C-P}$ = 3.0 Hz), 138.6 (d, $^1J_{C-P}$ = 78.9 Hz), 135.1 (d, $^3J_{C-P}$ = 14.7 Hz), 132.3 (d, $^2J_{C-P}$ = 10.3 Hz), 131.9 (d, $^4J_{C-P}$ = 2.5 Hz), 131.7, 131.2 (d, $^1J_{C-P}$ = 108.8 Hz), 130.1, 129.0, 128.9, 128.21 (d, $^3J_{C-P}$ = 11.8 Hz), 128.20, 113.3, 55.3, 37.8, 7.5; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C) δ 21.6; IR (neat) 3057, 1664, 1596,1510, 1438, 1315, 1257, 1219, 1192, 1164, 1115, 1024, 908 cm^{-1}; MS (70 eV, EI) m/z (%) 494 (M^+, 8.17), 135 (100). TOF HRMS (EI) calcd for $C_{31}H_{27}O_4P$ (M^+) 494.1647, found 494.1656.

*(Z)-3-(Diphenylphosphoryl)-1-(4-methoxyphenyl)-2-phenylhexa-2,5-diene-1,4-dione (**10**).* To a stirred solution of **3e** (49 mg, 0.10 mmol) in CH_3CN (2 mL) was added 1 equiv of NBS (18 mg) at 30 °C. After it was stirred for 30 min, to the resulting mixture was added 3 equiv of Et_3N (0.042 mL) by syringe and the temperature was raised to 80 °C. After the mixture was stirred for 3 h (monitored by TLC), 10 mL of chloroform was added to quench the reaction; after that, the mixture was extracted with three 3 mL portions of H_2O (in order to

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get rid of pyrrolidine-2,5-dione). The organic layers were dried over anhydrous $MgSO_4$. After filtration and removal of the solvent in vacuo, the residues were purified with flash silica chromatography (petroleum ether/ethyl acetate 4/1 v/v) to give the product **10** (40 mg, 0.081 mmol, 82%) as an oil: ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.75−7.84 (m, 4H), 7.72 (d, J = 8.0 Hz, 2H), 7.43−7.52 (m, 4H), 7.35−7.42 (m, 4H), 7.27−7.32 (m, 3H), 6.64 (d, J = 8.4 Hz, 2H), 5.95 (d, J = 16.8 Hz, 1H), 5.80 (dd, ^1J = 17.6 Hz, ^2J = 10.0 Hz, 1H), 5.39 (d, J = 10.4 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C) δ 195.3 (d, $^2J_{C-P}$ = 10.3 Hz), 192.1 (d, $^3J_{C-P}$ = 6.0 Hz), 163.4, 158.9 (d, $^4J_{C-P}$ = 3.8 Hz), 135.84 (d, $^4J_{C-P}$ = 1.8 Hz), 135.80 (d, $^1J_{C-P}$ = 80.8 Hz), 135.1 (d, $^3J_{C-P}$ = 14.0 Hz), 132.3 (d, $^2J_{C-P}$ = 10.7 Hz), 131.9 (d, $^4J_{C-P}$ = 2.5 Hz), 131.7, 131.2 (d, $^1J_{C-P}$ = 107.3 Hz), 130.6, 130.1, 128.9, 128.8, 128.5, 128.2 (d, $^3J_{C-P}$ = 13.1 Hz), 113.4, 55.3; ^{31}P NMR (162 MHz, $CDCl_3$, 25 °C) δ 22.7; IR (neat) 3057, 1664, 1597, 1510, 1487, 1438, 1398, 1316, 1251, 1193, 1164, 1116, 1022, 925 cm^{-1}; MS (70 eV, EI) m/z (%) 492 (M^+, 42.18), 135 (100). TOF HRMS (EI) calcd for $C_{31}H_{25}O_4P$ (M^+) 492.1490, found 492.1494.

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra for compounds **3**, **7m**, and **8**−**10** and figures and CIF files giving structures and X-ray crystallographic data for **3a**, **7m**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

[§]Professor Huang passed away on March 6, 2010. He was fully in charge of this project. Professor Luling Wu is helping to finish all the projects with assistance from Professor Shengming Ma.

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