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Graphical Abstract

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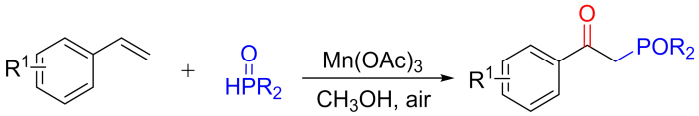

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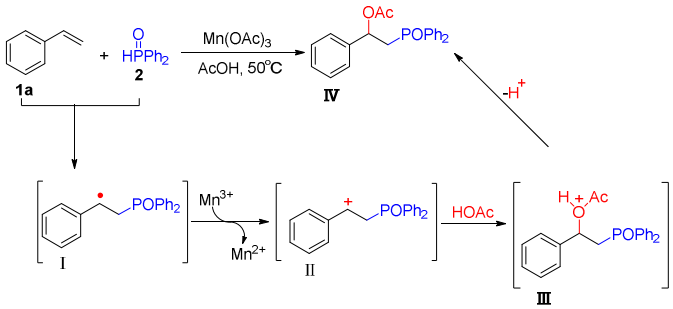
ABSTRACT

Direct radical oxyphosphorylation of styrenes with diarylphosphine oxides and dialkyl phosphites mediated by $Mn(OAc)_3$ is described. The solvent played a key role in this selective difunctionalization reaction.

1. Introduction

Difunctionalization reaction involving alkenes has been of considerable interest in organic synthesis due to advantages such as its high efficiency, atom and step economy.[1] One of the most significant among this type of reactions are those involving a phosphorus-containing functional group since the resultant product can be easily transformed into other compounds such as β-keto, β-amino, and β-hydroxyphosphonates.[2] Several methods of C-P bond formation have been described in literature,[3,4] however, reports on the difunctionalization of alkenes involving a phosphorus-containing group are few.[5] In 2011, Ji's group described the first example involving transition metal-catalyzed oxyphosphorylation of alkenes with dioxygen and H-phosphonates[5g]. More recently, our group reported a Manganese(III)-mediated acetoxyphosphorylation of alkenes[6] with diphenylphosphine oxide or dimethyl phosphite leading exclusively to acetoxyphosphorylation products. The method proceeded via a phosphorus-centred radical addition to the alkene to form (I), subsequent oxidation and solvent (HOAc) attack tandem process, followed by deprotonation gave compound (IV) (Scheme 1). The $Mn(OAc)_3$/HOAc system employed possesses a high oxidative potential as it oxidized both diphenylphosphine oxide (or dimethyl phosphite) and the intermediate carbon-centred radical (I) to the corresponding phosphorus-centered radical and carbocation (II) respectively. We envisioned that if the oxidizing ability of $Mn(OAc)_3$ can be controlled by changing some reaction conditions involved in the process described in Scheme 1, the resultant intermediate carbon-centered radical obtained from the initial addition of the phosphorus-centered radical might be prevented from further oxidation. This could then be subjected to other radical transformations thus achieving a new type of selective difunctionalization of alkenes. Herein, we report a new protocol involving oxyphosphorylation of alkenes in the presence of $Mn(OAc)_3$ and air. In this reaction, both H-phosphonates and diarylphosphine oxides were tolerated giving the corresponding products.



Scheme 1. Plausible mechanism of acetoxyphosphorylation of styrene

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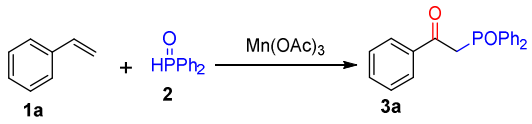
2. Results and Discussion

To test our hypothesis, the reaction between styrene (**1a**) and diphenylphosphine oxide (**2**) was carried out in the presence of $Mn(OAc)_3$ under aerobic conditions. At the outset, polar solvents such as MeOH, *t*-BuOH, CH_3CN, THF, DMF, and DMSO were used. To our delight, a new product, 2-(diphenylphosphoryl)-1-phenylethanone (**3a)** was observed in all cases (Table 1, entries 1-6). MeOH, *t*-BuOH and CH_3CN were the best solvents among which MeOH was selected for further optimization. Subsequently, the reaction temperature, time and ratio of styrene/$HP(O)Ph_2$/$Mn(OAc)_3$ were screened. The best result was obtained when a ratio of styrene/$HP(O)Ph_2$/$Mn(OAc)_3$ (1:2:2) was reacted in MeOH for 1 h at 30°C (Table 1, entry 7). It was interesting that the yield of product obtained under air was higher than in O_2 atmosphere (Table 1, entry 10); this implied that the concentration of oxygen has an important influence on the outcome of reaction.

Table 1. Optimization of the reaction conditions



Entry	Slovent	**1a**:**2**:$Mn(OAc)_3$	Temp./°C	Time/min	Yield/%[a]
1	CH_3OH	1:2:2	50	30	67
2	*t*-BuOH	1:2:2	50	30	65
3	CH_3CN	1:2:2	50	30	60
4	THF	1:2:2	50	30	43
5	DMF	1:2:2	50	30	30
6	DMSO	1:2:2	50	30	32
7	CH_3OH	1:2:2	30	60	75
8	CH_3OH	1:2:2	70	20	60
9	CH_3OH	1:1.8:1.8	30	60	64
10	CH_3OH	1:2:2	30	60	50[b]

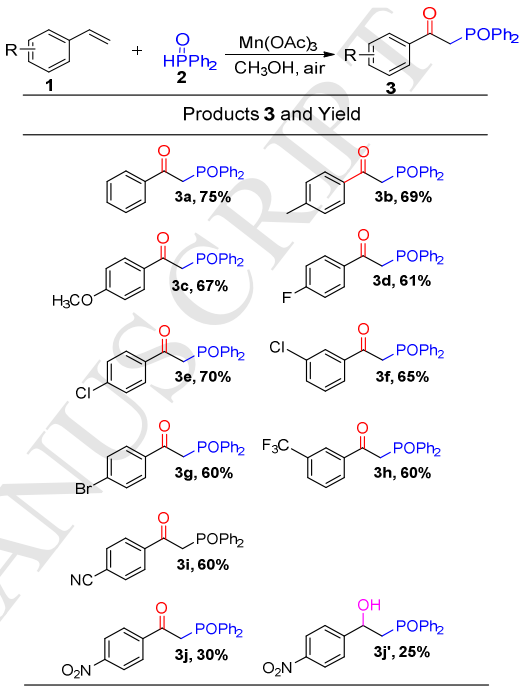
[a] Isolated yield;

[b]The reaction was carried out under O_2 atmosphere.

The optimal reaction conditions obtained above were applied to different set of styrenes to evaluate the scope of this reaction. In general, electronic effect had less influence on the yield as both electron-withdrawing and electron-donating styrene all afforded the expected 2-(diphenylphosphoryl)-1-arylethanones in yields ranging from 60−75% (Table 2, **3a-i**). However, the reaction of 4-nitrostyrene with **2** produced a mixture of 2-(diphenylphosphoryl)-1-(4-nitrophenyl)ethanone **(3j)** and (2-hydroxy-2-(4-nitrophenyl)ethyl)diphenylphosphine oxide (**3j'**) in 55% combined yield. The strong electron-withdrawing group NO_2 could be responsible for the competitive reaction pathways involved.

Considering the success of the reaction with diphenylphosphine oxide **2**, the reaction with dialkylphosphites was also tested. With, dimethylphosphite (**4**), the best condition was observed in MeOH for 1 hour at 70°C. The results showed that styrenes bearing either electron-donating or electron-withdrawing groups on the phenyl ring all afforded oxyphosphorylation products in moderate to good yields (up to 69%, Table 3, **5a-i**). Interestingly, the reaction of 4-nitrostyrene in this case yielded only a major product **5j** in 50% yield thus indicating that radical reaction is sensitive to the nature of the phosphorus radical.

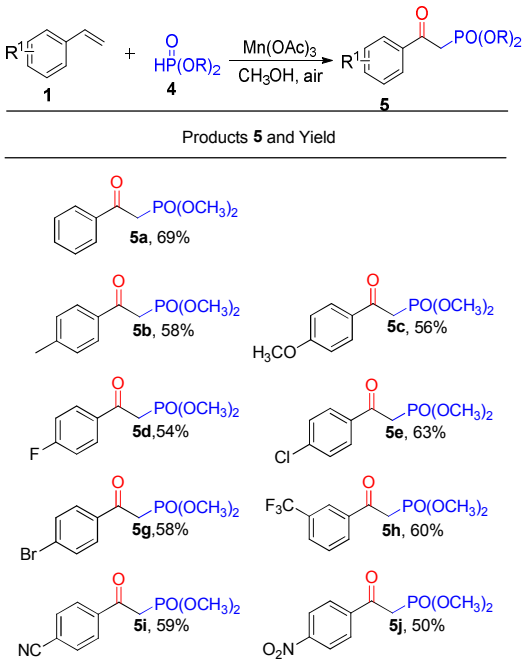
Table 2. Reactions of styrenes **1**and diphenylphosphine oxide **2**[a, b]



[a] Reaction conditions: styrene (1.0 mmol), $HP(O)Ph_2$ (2.0 mmol), $Mn(OAc)_3$ (2.0 mmol) in MeOH (10 mL), 30 °C, 60 min;

[b] Isolated yield.

Table 3. Reactions of styrenes **1**and dialkylphosphites **4**[a, b]



[a] Reaction conditions: styrene (1.0 mmol), $HPO(OR)_2$ (2.0 mmol), $Mn(OAc)_3$ (2.0 mmol) in CH_3OH (10 mL), 70 °C, 60 min; [b] Isolated yield.

Moving further, the effects of α- or β-substituents on styrene were studied. The reactions of both α-methylstyrene (**1k**) and α-phenylstyrene (**1m**) with diphenylphosphine oxide (**2**) afforded the hydroxyphosphorylation products **3k** and **3m** in 73% and 74% yields respectively (Table 4). Oxyphosphorylation products were not observed in this case due to the presence of α-substituents. However, in a situation where the α-substituent could be lost easily, oxyphosphorylation products were obtained as is the case with α-bromostyrene (**1l**); the reaction with **2** and **4** produced **3a** and **5a** respectively in moderate yields. Surprisingly, the reaction of **1m** with dimethylphosphite (**4**) yielded alkenylphosphonate **5m** in 75% yield. Product **5m** could have been derived from the dehydration of the corresponding hydroxyphosphonylation intermediate. Furthermore, the reactions of both β-methylstyrene (**1n**) and β-phenylstyrene (**1p**) with **2** gave the corresponding hydroxyphosphorylation products **3n** (73%) and **3p** (65%) respectively (Table 4). The reaction of **1n** with **4** gave benzoic acid rather than the expected product **5n** due to the oxidation of **1n**. Also, the reactions of β-bromostyrene (**1o**) with **2** and **4** both led to addition-elimination products **3o** and **5o** via the phosphorus-centred radical addition to the terminal C=C double bond, followed by elimination of bromo radical to form alkenylphosphonylation products. The attack of oxygen on intermediate carbon radical is not observed in this case. Based on the results above, the reactions of α- or β-substituted styrenes with diphenylphosphine oxide (**2**) and dimethylphosphite (**4**) gave diverse products depending on the nature and position of substituents. Finally, reactions involving several non-conjugated terminal alkenes were carried out giving exclusively hydrophosphorylation products **3q-t** in good yields (Table 4).

To confirm the reaction proceeded via radical process, a control experiment has been done, and the result indicates that the reaction of styrene with diphenylphosphine oxide can be inhibited by addition of 1,1-diphenyl styrene (Scheme 2). A mechanism for the reactions of alkenes with diphenylphosphine oxide (**2**) and dialkyl phosphites (**4**) is proposed in Scheme 2. A phosphorus-centred radical **6** derived from **2** or **4** selectively adds to the terminal end of C=C double bond of **1** to form a carbon-centered intermediate radical **7**. When R is an alkyl, **7** becomes reactive thus abstracting a proton to give hydrophosphorylation products. On the other hand, if R is an aryl, **7** could be stabilized making it to interact with O_2 to form peroxy radical **8**; subsequent proton abstraction and dehydration leads to products **3** or **5**.

3. Conclusion

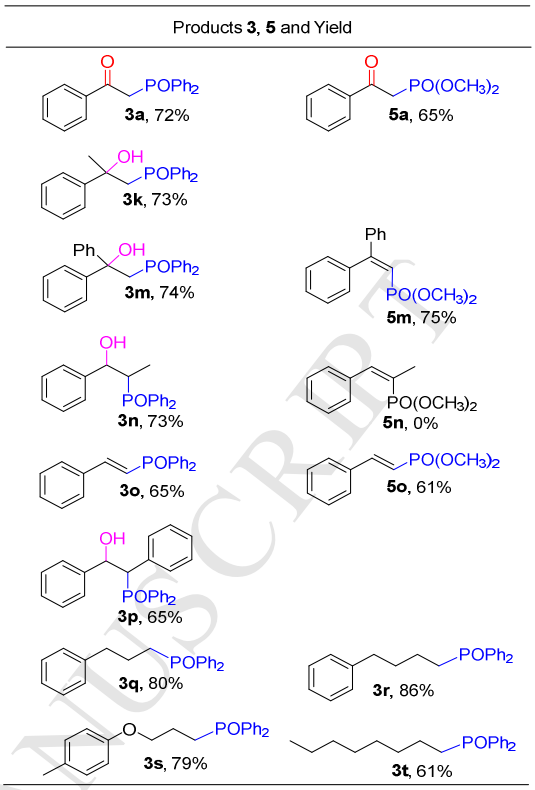
In conclusion, a new general protocol of $Mn(OAc)_3$-mediated oxyphosphorylation of styrenes in air has been developed. The solvent played an important role in this reaction leading exclusively to oxyphosphorylation products. Advantages of this methodology include mild reaction conditions, wide scope of substrates, and the need for no further additives or oxidant. Both diarylphosphine oxides and dialkyl phosphites were suitable under this transformation. This protocol provides a new route to β-ketophosphonates which can be easily transformed into other compounds such as α,β-unsaturated carbonyl compounds, chiral β-amino and β-hydroxy phosphonic acids etc.

4. Experimental Section

4.1. General

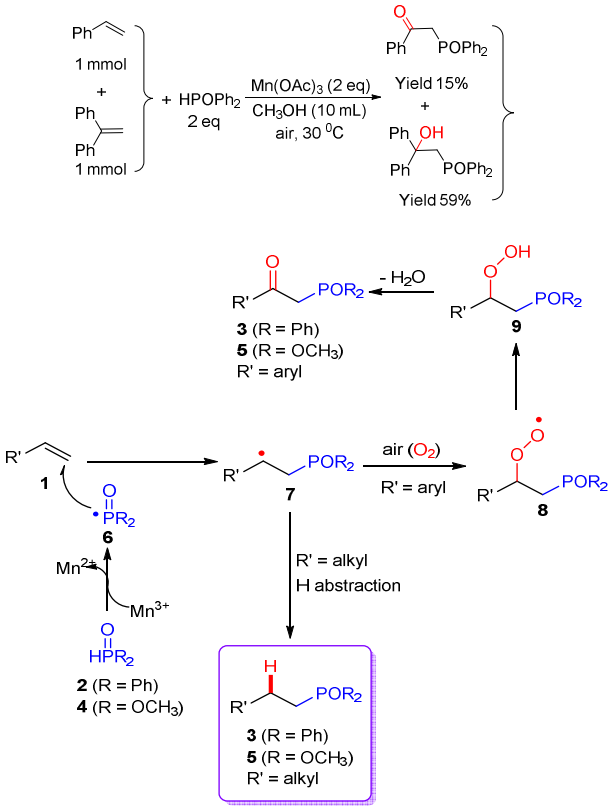
^{1}H NMR(400 MHz or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were determined with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard or 85% H_3PO_4 as external standard for ^{31}P NMR (162 MHz). Chemical shifts were

Table 4. Reactions of α- and β-substituted styrenes **1** with diphenylphosphine oxide **2** and dimethyl phosphite **4**[a,b]



[a] Reaction conditions: styrene (1.0 mmol), $HP(O)Ph_2$ (2.0 mmol), $Mn(OAc)_3$ (2.0 mmol) in MeOH (10 mL), 30 °C, 60 min; styrene (1.0 mmol), $HP(O)(OCH_3)_2$ (2.0 mmol), $Mn(OAc)_3$ (2.0 mmol) in CH_3OH (10 mL), 70 °C, 60 min;

[b] Isolated yield.



Scheme 2. Possible mechanism of oxyphosphorylation of alkenes

reported in ppm from internal TMS(δ), all coupling constants (J values) were reported in Hertz (Hz). High resolution mass spectra were recorded on a TOF machine (ESI). Column chromatography was performed with 300-400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted. All alkenes were purified by flash column chromatography (Al_2O_3) before use.

4.2. General procedure for the preparation of 2-(diphenylphosphoryl)-1-arylethanones3

*Typical procedure for the preparation of 2-(diphenylphosphoryl)-1-phenylethanone (**3a**).*To a solution of methanol (10 mL), styrene (0.11 g, 1.0 mmol) and diphenylphosphine oxide (0.40 g, 2.0 mmol) was added $Mn(OAc)_3$ (0.54 g, 2.0 mmol) over 30 minutes at 30°C, and the mixture was stirred for another 30 minutes to complete the reaction. Then, the solvent was removed under vacuum. To the residue was added water (20 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic fractions were dried over anhydrous Na_2SO_4, and concentrated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, petroleum ether/EtOAc/CH_2Cl_2 (10:1:1)) to give pure 2-(diphenylphosphoryl)-1-phenylethanone (**3a**).

4.3 Characterization

*2-(Diphenylphosphoryl)-1-phenylethanone (**3a**)*[7]

White solid, mp 160−161 °C, 75% yield (240.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.98 (d, J = 7.4 Hz, 2H), 7.84−7.78 (m, 4H), 7.54−7.40 (m, 9H), 4.15 (d, J = 15.3 Hz, 2H);^{13}C NMR (75 MHz, $CDCl_3$):δ192.8 (d, J = 5.2 Hz), 136.9, 133.6, 132.6, 132.2, 131.1 (d, J = 9.8 Hz), 129.2, 128.7, 128.5, 43.2 (d, J = 57.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$):δ26.91; HRMS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for $C_{20}H_{18}O_2P$ 321.1044, found 321.1047.

*2-(Diphenylphosphoryl)-1-(p-tolyl)ethanone (**3b**)*[8]

White solid, mp 152−153°C, 65% yield (217.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.89 (d, J = 7.2 Hz, 2H), 7.76−7.85 (m, 4H), 7.43−7.54 (m, 6H), 7.21 (d, J = 7.2 Hz, 2H), 4.12 (d, J =15.2 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ192.3, 144.6, 134.4, 132.4, 132.1, 131.4, 131.1 (d, J = 9.7Hz), 129.3 (d, J = 17.6 Hz), 128.5 (d, J = 12.3 Hz), 43.1 (d, J = 58.4 Hz), 21.6; MS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for $C_{21}H_{20}O_2P$ 335.1, found 335.1.

*2-(Diphenylphosphoryl)-1-(4-methoxyphenyl)ethanone (**3c**)* [9]

White solid, mp 147−148 °C, 62% yield (217.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$):δ7.99 (d, J = 8.8 Hz, 2H), 7.87−7.76 (m, 4 H),7.55–7.43 (m, 6 H),6.89(d, J = 8.7 Hz, 2H), 4.09 (d, J = 15.3 Hz, 2H), 3.85 (s, 3 H);^{13}C NMR (100 MHz, $CDCl_3$): δ191.0 (d, J = 5.3 Hz), 164.0, 132.6, 132.1 (d, J = 2.3 Hz), 131.8, 131.2 (d, J = 9.7 Hz), 130.2, 128.6 (d, J = 12.2 Hz), 113.7, 55.5, 43.3 (d, J =58.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$):δ27.13; MS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for $C_{21}H_{20}O_3P$ 351.1, found 351.1.

*2-(Diphenylphosphoryl)-1-(4-fluorophenyl)ethanone (**3d**)*

White solid, mp 156−157 °C, 61% yield (206.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.02 (dd, J = 8.4, 5.5 Hz, 2H), 7.80 (dd, J = 11.8, 7.5 Hz, 4H), 7.55−7.41 (m, 6H), 7.07 (t, J = 8.5 Hz, 2H), 4.11(d, J = 15.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):δ191.2 (d, J = 5.6 Hz), 166.0 (d, J = 256.0 Hz), 133.4 (d, J = 2.8 Hz), 132.3, 132.2 (d, J = 2.8 Hz), 132.1 (d, J = 9.6 Hz), 131.3, 131.1 (d, J = 9.8 Hz), 128.7 (d, J = 12.4 Hz), 115.6 (d, J = 22.0 Hz), 43.5 (d, J = 56.9 Hz);^{31}P NMR (162 MHz, $CDCl_3$): δ26.81; HRMS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for$C_{20}H_{17}FO_2P$ 339.0950, found 339.0944.

*1-(4-Chlorophenyl)-2-(diphenylphosphoryl)ethanone (**3e**)*[10]

White solid, mp 159−160 °C, 70% yield (247.8 mg); ^{1}H NMR (400 MHz, DMSO-d_6): δ8.02−7.97 (m, 2H), 7.86−7.79 (m, 4H), 7.59−7.48 (m, 8H), 4.54 (d, J = 14.6 Hz, 2H);^{13}C NMR (100 MHz, DMSO-d_6):δ192.9 (d, J = 6.4 Hz), 139.0, 136.2, 133.7 (d, J = 101.4 Hz), 132.3 (d, J = 2.6 Hz), 131.4, 131.1 (d, J = 9.7 Hz),129.1 (d, J = 5.1 Hz), 129.0, 41.9 (d, J = 59.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$):δ26.67; HRMS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for $C_{20}H_{17}ClO_2P$ 355.0655, found 355.0664.

*1-(3-Chlorophenyl)-2-(diphenylphosphoryl)ethanone (**3f**)*

White solid, mp 158−159 °C, 65% yield (230.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.81 (d, J = 12.0 Hz, 2H), 7.70 (dd, J = 11.2, 8.0 Hz, 4H), 7.43–7.34 (m, 7H), 7.29–7.24 (m, 1H), 4.03 (d, J = 14.9 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$):δ191.7 (d, J = 5.6 Hz), 138.5, 134.82, 133.5, 132.34 (d, J = 2.4 Hz), 131.1, 131.0, 129.9, 128.9, 128.7 (d, J = 12.3 Hz), 127.7, 43.4 (d, J = 57.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ26.80; HRMS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for $C_{20}H_{17}ClO_2P$ 355.0655, found 355.0670.

*1-(4-Bromophenyl)-2-(diphenylphosphoryl)ethanone (**3g**)*

White solid, mp 144−145 °C,60 % yield (238.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.91−7.84 (m, 2H), 7.83−7.74 (m, 4H), 7.59−7.50 (m, 4H), 7.43−7.49 (m, 4H), 4.10 (d, J = 15.2 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$):δ191.9 (d, J = 5.6 Hz), 135.7, 132.3 (d, J = 2.8 Hz), 131.9, 131.1 (d, J = 9.8 Hz), 130.9, 129.1, 128.7 (d, J = 12.3 Hz), 43.6 (d, J = 56.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.90; HRMS (ESI-TOF) *m/z*: (M+H)$^+$ Calcd for $C_{20}H_{17}BrO_2P$ 399.0150, found 399.0177.

*2-(Diphenylphosphoryl)-1-(3-(trifluoromethyl)phenyl)ethanone (**3h**)*

White solid, mp 173−174°C, 60% yield (232.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$):δ 8.26 (d, J = 7.8 Hz, 1H), 8.18−8.14 (m, 1H), 7.84−7.75 (m, 5H), 7.58−7.46 (m, 7H), 4.17 (d, J = 15.3 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$):δ191.3 (d, J = 5.5 Hz), 136.9, 132.3, 131.9 (d, J = 2.6 Hz), 130.6, 130.5, 129.4 (q, J =3.5 Hz), 128.8, 128.3, 128.2, 125.3 (q, J = 3.8 Hz), 43.2 (d, J = 56.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ26.51; HRMS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for $C_{21}H_{17}F_3O_2P$ 389.0918, found 389.0941.

*1-(4-Cyanophenyl)-2-(diphenylphosphoryl)ethanone(**3i**)*

White solid, mp 169−170 °C, 60% yield (207.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.13 (d, J = 8.2 Hz, 2H), 7.79 (dd, J = 12.0, 7.5 Hz, 4H), 7.72 (d, J = 8.2 Hz, 2H), 7.57−7.53 (m, 2H), 7.51−7.46 (m, 4H), 4.15 (d, J = 15.0 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$):δ191.8 (d, J = 5.8 Hz), 139.8, 132.5 (d, J = 2.7 Hz), 132.4, 131.0 (d, J = 9.8 Hz), 129.8, 128.8 (d, J = 12.4 Hz), 117.9, 116.7, 44.1 (d, J = 55.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.50; HRMS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for$C_{21}H_{17}NO_2P$346.0997, found 346.0990.

*2-(Diphenylphosphoryl)-1-(4-nitrophenyl)ethanone (**3j**)*[11]

Yellow solid, mp 163−164 °C,30% yield (109.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.26 (d, J = 8.9 Hz, 2H), 8.20 (d, J = 8.9 Hz, 2H), 7.83–7.76 (m, 4H), 7.56 (td, J = 7.2, 1.3 Hz, 2H), 7.52–7.47 (m, 4H), 4.17 (d, J = 15.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):δ191.6 (d, J = 5.8 Hz), 150.5, 141.2, 132.5 (d, J = 2.9 Hz), 131.9, 131.0 (d, J = 9.9 Hz), 130.5, 128.9 (d, J = 12.4 Hz), 123.7, 44.3 (d, J = 55.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$):δ26.55; MS (ESI-TOF) *m/z*: (M+H)$^+$Calcd for $C_{20}H_{19}NO_4P$ 366.1, found 366.1.

*2-(Diphenylphosphoryl)-1-(4-nitrophenyl)ethanol(**3j'**)*

Yellow solid, mp 170−171 °C, 25% yield (92.1 mg); ^{1}H NMR

(400 MHz, $CDCl_3$): δ8.11 (d, J = 8.7 Hz, 2H), 7.75 (dd, J = 11.0, 7.7 Hz, 2H), 7.67 (dd, J = 11.8, 7.5 Hz, 2H), 7.60–7.55 (m, 1H), 7.54–7.46 (m, 5H), 7.43 (dt, J = 7.2, 3.7 Hz, 2H), 5.72 (s, 1H), 5.29 (t, J = 9.5 Hz, 1H), 2.81–2.67 (m, 1H), 2.65–2.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$):δ151.4 (d, J = 12.5 Hz), 147.2, 132.4 (d, J = 2.4 Hz), 132.3 (d, J = 2.5 Hz), 130.8 (d, J = 9.5 Hz), 130.5 (d, J = 9.8 Hz), 129.0 (d, J = 4.1 Hz, 128.8 (d, J = 12 Hz), 126.5, 123.7, 68.4, 39.0 (d, J = 68.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ33.80; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{20}H_{19}NO_4P$ 368.1052, found 368.1061.

*2-(Diphenylphosphoryl)-1-methyl-1-phenyl)ethanol(**3k**)*[12]

White solid, mp 178−179°C, 73% yield (245.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.74 (dd, J = 11.1, 7.4 Hz, 2H), 7.54–7.46 (m, 3H), 7.37–7.30 (m, 5H), 7.24–7.19 (m, 2H), 7.07 (t, J = 7.3 Hz, 2H), 7.01 (t, J = 7.1 Hz, 1H), 5.05 (s, 1H), 2.92 (d, J = 9.3 Hz, 2H), 1.60 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$):δ146.7 (d, J = 5.9 Hz), 132.0 (d, J = 2.6 Hz), 131.2 (d, J = 2.7 Hz), 130.3 (d, J = 9.6 Hz), 128.8 (d, J = 11.7 Hz), 128.2 (d, J = 12.1 Hz), 127.8, 126.6, 124.8, 74.2 (d, J = 5.3 Hz), 42.3 (d, J = 69.1 Hz), 32.9 (d, J = 9.5 Hz);^{31}P NMR (162 MHz, $CDCl_3$):δ32.74; MS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{21}H_{22}O_2P$ 337.1, found 337.1.

*2-(Diphenylphosphoryl)-1,1-diphenyl)ethanol(**3m**)*[12]

White solid, mp 183−184 °C, 74% yield (294.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.05–7.97 (m, 2H), 7.60 (s, 3H), 7.51 (dd, J = 11.3, 7.4 Hz, 2H), 7.29 (t, J = 7.0 Hz, 1H), 7.24–7.14 (m, 4H), 7.10–7.01 (m, 6H), 6.89–6.84 (m, 2H), 5.51 (d, J = 7.2 Hz, 1H), 5.17 (s, 1H), 3.64 (d, J = 8.0 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$):δ141.2 (d, J = 12.2 Hz), 132.2 (d, J = 2.4 Hz), 131.9 (d, J= 2.9 Hz), 131.6 (d, J = 2.5 Hz), 131.3 (d, J = 6.9 Hz), 131.1 (d, J = 8.7 Hz), 130.8 (d, J = 9.1 Hz), 129.1 (d, J = 11.4 Hz), 128.3 (d, J = 12.0 Hz), 127.7, 127.2, 127.1, 125.9, 72.6, 53.2(d, J = 66.6 Hz);^{31}P NMR (162 MHz, $CDCl_3$):δ33.24; MS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{26}H_{24}O_2P$ 399.1, found 399.1.

*2-(Diphenylphosphoryl)-2-methyl-1-phenyl)ethanol(**3n**)*[13]

White solid, mp 189−190°C, 70% yield (235.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.75 (d, J = 6.5 Hz, 2H), 7.38–7.27 (m, 4H), 7.21–7.13 (m, 4H), 7.12–7.02(m, 5H), 4.62 (d, J = 30.7 Hz, 1H), 3.03–2.91 (m, 1H), 1.05 (dd, J = 16.6, 7.5 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$):δ139.3 (d, J = 4.0 Hz), 135.4 (d, J = 95.4 Hz), 132.2 (d, J = 8.4 Hz), 130.9 (d, J = 2.4 Hz), 130.7 (d, J = 4.2 Hz), 130.6, 128.1 (d, J = 11.1 Hz), 127.9, 127.5 (d, J = 11.3 Hz), 126.7, 53.7 (d, J = 3.0 Hz), 37.2 (d, J = 70.3 Hz), 16.7;^{31}P NMR (162 MHz, $CDCl_3$):δ37.54; MS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{21}H_{22}O_2P$ 337.1, found 337.1.

*(E)-2-(Diphenylphosphoryl)-1-phenyl)ethylene (**3o**)*[14]

White solid, mp 169−170 °C, 68% yield (206.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.76 (dd, J = 11.9, 7.4 Hz, 4H), 7.58–7.43 (m, 9H), 7.41–7.32 (m, 3H), 6.84 (dd, J = 22.3, 17.4 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$):δ147.6 (d, J = 3.6 Hz), 135.1 (d, J = 17.9 Hz), 133.5, 132.5, 131.9 (d, J = 2.7 Hz), 131.4 (d, J = 10.0 Hz), 130.1, 128.9, 128.6 (d, J = 12.2 Hz), 127.8, 119.8, 118.7;^{31}P NMR (162 MHz, $CDCl_3$):δ24.48; MS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{20}H_{18}OP$ 305.1, found 305.1.

*2-(Diphenylphosphoryl)-1,2-diphenyl)ethanol (**3p**)*[15]

White solid, mp248−249°C, 65% yield (258.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.06–7.96 (m, 2H), 7.63–7.56 (m, 3H), 7.51 (dd, J = 11.3, 7.4 Hz, 2H), 7.29 (t, J = 7.0 Hz, 1H), 7.24–7.14 (m, 4H), 7.11–7.01 (m, 6H), 6.90–6.84 (m, 2H), 5.51 (d, J = 7.2 Hz, 1H), 5.17 (s, 1H), 3.65 (d, J = 8.0 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$): δ141.2 (d, J = 12.2 Hz), 132.2 (d, J = 2.4 Hz), 131.9 (d, J = 2.9 Hz), 131.6 (d, J = 2.5 Hz), 131.3 (d, J = 6.9 Hz), 131.0 (d, J = 8.7 Hz), 130.7 (d, J = 9.1 Hz), 129.1 (d, J = 11.4 Hz), 128.3 (d, J = 12.0 Hz), 127.7, 127.2, 127.1, 125.9, 72.6, 53.2 (d, J = 66.6 Hz);^{31}P NMR (162 MHz, $CDCl_3$):δ36.70; MS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{26}H_{24}O_2P$ 399.1, found 399.1.

*Diphenyl(3-phenylpropyl)phosphine oxide (**3q**)*[16]

White solid, mp 116.5−117.0 °C, 80% yield (256.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.72–7.63 (m, 4H), 7.56–7.38 (m, 7H), 7.25–7.22 (m, 1H), 7.20–7.16 (m, 1H), 7.11 (d, J = 6.9 Hz, 2H), 2.76–2.68 (m, 2H), 2.39–2.15 (m, 2H), 1.97–1.94 (m, 2H);^{13}C NMR (75 MHz, $CDCl_3$):δ140.8, 131.7, 130.7 (d, J = 9.0 Hz), 128.7, 128.6, 128.5, 128.4, 126.1, 36.6 (d, J = 14.8 Hz), 28.9 (d, J = 71.9 Hz), 23.0;^{31}P NMR (162 MHz, $CDCl_3$):δ32.46; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{21}H_{22}OP$ 321.1408, found 321.1416.

*Diphenyl(4-phenylbutyl)phosphine oxide (**3r**)*[17]

White solid, mp 92−93°C, 86% yield (287.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.75–7.69 (m, 4H), 7.54–7.43 (m, 6H), 7.26–7.09 (m, 5H), 2.61–2.56 (m, 2H), 2.32–2.24 (m, 2H),1.75–1.67 (m, 4H);^{13}C NMR (75 MHz, $CDCl_3$):δ141.9, 133.7, 132.4, 131.7, 130.8 (d, J = 8.9 Hz), 128.6 (d, J = 11.3 Hz), 128.3, 125.8, 35.4, 32.7 (d, J = 14.2 Hz), 29.6 (d, J = 71.7 Hz), 21.2;^{31}P NMR (162 MHz, $CDCl_3$):δ32.38; MS (ESI-TOF) *m/z*: $(M+H)^+$ Calcd for $C_{22}H_{24}OP$ 335.1, found 335.1.

*Diphenyl 3-(p-tolyloxy)propyl)phosphine oxide (**3s**)*[17]

White solid, mp 113−114°C, 79% yield (276.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.82–7.67 (m, 4H), 7.55–7.43 (m, 6H), 7.05 (d, J = 8.1 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 4.00–3.92 (m, 2H), 2.54–2.42 (m, 2H), 2.27 (s, 3H), 2.16–2.02 (m, 2H);^{13}C NMR (75 MHz, $CDCl_3$):δ156.5, 132.8 (d, J = 98.9 Hz), 131.8, 130.8 (d, J = 9.1 Hz), 130.0, 129.9, 128.7 (d, J = 11.5 Hz), 114.3, 67.6 (d, J = 14.3 Hz), 26.4 (d, J = 72.8 Hz), 21.2 (d, J = 102.8 Hz);^{31}P NMR (162 MHz, $CDCl_3$):δ32.55; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{22}H_{24}O_2P$ 351.1514, found 351.1513.

*Diphenyloctylphosphine oxide (**3t**)*[17]

White solid, mp57−58°C, 61% yield (191.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.78–7.70 (m, 4H), 7.53–7.44 (m, 6H), 2.34–2.18 (m, 2H), 1.70–1.54 (m, 2H), 1.43–1.33 (m, 2H),1.28–1.17 (m, 8H), 0.85 (t, J = 6.7 Hz, 3H);^{13}C NMR (75 MHz, $CDCl_3$):δ132.8 (d, J = 97.9 Hz), 131.6 , 130.6 (d, J = 9.0 Hz), 128.5 (d, J = 11.3 Hz), 31.6, 30.8 (d, J = 14.2 Hz), 29.5 (d, J = 72.1 Hz), 28.9, 22.4, 21.2 (d, J = 2.7 Hz), 21.1, 13.9;^{31}P NMR (162 MHz, $CDCl_3$):δ32.96; MS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{20}H_{27}OP$ 315.2, found 315.2.

Preparation of dimethyl (2-oxo-2-arylethyl)phosphonates 5. *Typical procedure for the preparation of dimethyl (2-oxo-2-phenylethyl)phosphonate (**5a**).* To a solution of methanol (10 mL), styrene (0.11 g, 1.0 mmol) and dimethylphosphite (0.22 g, 2.0 mmol) was added $Mn(OAc)_3$ (0.54 g, 2.0 mmol) over 30 minutes at 70^{o}C, and the mixture was stirred for another 30 minutes to complete the reaction. Then, the solvent was removed under vacuum. To the residue was added water (20 mL) and extracted with ethyl acetate (10 mL× 3). The combined organic fractions were dried over anhydrous Na_2SO_4, and concentrated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, petroleum ether/EtOAc/CH_2Cl_2(10:1:1)) to give pure dimethyl (2-oxo-2-phenylethyl)phosphonate (**5a**).

*Dimethyl (2-oxo-2-phenylethyl)phosphonate (**5a**)*[18]

Colorless liquid; 69% yield (157.4 mg); ^{1}H NMR (400 MHz,

$CDCl_3$): δ8.04–7.97 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.49 (t, J= 7.7 Hz, 2H), 3.79 (d, J = 11.2 Hz, 6H), 3.65 (d, J = 22.6 Hz, 2H);^{13}C NMR (75 MHz, $CDCl_3$):δ191.7 (d, J = 6.6 Hz),136.3 (d, J = 2.5 Hz), 133.8, 128.9,128.7, 53.2 (d, J = 6.5 Hz), 37.4 (d, J = 131.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$):δ22.80; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{10}H_{14}O_4P$ 229.0630, found 229.0635.

*Dimethyl (2-oxo-2-(p-tolyl)ethyl)phosphonate (**5b**)*[18]

^{1}H NMR (400 MHz, $CDCl_3$):δ7.98 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 7.5 Hz, 2H), 3.86 (d, J = 11.2 Hz, 6H), 3.70 (d, J = 22.6 Hz, 2H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):δ190.8 (d, J = 6.6 Hz), 144.4, 133.5 (d, J = 2.5 Hz), 128.9, 128.7, 52.7 (d, J = 6.5 Hz), 36.9 (d, J = 131.4 Hz), 21.2;^{31}P NMR (162 MHz, $CDCl_3$):δ23.08; MS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{11}H_{16}O_4P$ 243.1, found 243.0.

*Dimethyl (2-(4-methoxyphenyl)-2-oxoethyl)phosphonate (**5c**)*[19]

^{1}H NMR (400 MHz, $CDCl_3$): δ7.99 (d, J = 8.9 Hz, 2H), 6.95 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), 3.78 (d, J = 11.2 Hz, 6H), 3.60 (d, J = 22.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):δ189.6 (d, J = 6.5 Hz), 163.6, 130.9, 129.0 (d, J = 2.4 Hz), 113.4, 55.0, 52.6 (d, J = 6.5 Hz), 36.7 (d, J = 131.0 Hz);^{31}P NMR (162 MHz, $CDCl_3$):δ23.24; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{11}H_{16}O_5P$ 259.0735, found 259.0725.

*Dimethyl (2-(4-fluorophenyl)-2-oxoethyl)phosphonate (**5d**)*[19]

^{1}H NMR (400 MHz, $CDCl_3$):δ8.11–7.99 (m, 2H), 7.20–7.12 (m, 2H), 3.79 (d, J = 11.2 Hz, 6H), 3.62 (d, J = 22.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):δ189.7 (d, J = 6.5 Hz), 165.7 (d, J = 255 Hz), 132.3 (dd, J = 2.0, 3.0 Hz),131.3 (d, J = 9.6 Hz), 115.4 (d, J = 22.0 Hz), 52.7 (d, J = 6.6 Hz), 37.1 (d, J = 130.9 Hz);^{31}P NMR (162 MHz, $CDCl_3$):δ22.45; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{10}H_{13}FO_4P$ 247.0535, found 247.0530.

*Dimethyl (2-(4-chlorophenyl)-2-oxoethyl)phosphonate (**5e**)*[19]

Colorless liquid, 63% yield (165.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.96 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 3.79 (d, J = 11.2 Hz, 6H), 3.61 (d, J = 22.8 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$):δ190.6 (d, J = 6.6 Hz), 140.4, 134.7 (d, J = 2.2 Hz), 130.4, 129.0, 53.2 (d, J = 6.5 Hz), 37.6 (d, J = 130.7 Hz);^{31}P NMR (162 MHz, $CDCl_3$):δ22.42; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{10}H_{13}ClO_4P$ 263.0240, found 263.0238.

*Dimethyl (2-(4-bromophenyl)-2-oxoethyl)phosphonate (**5g**)*[19]

Colorless liquid, 58% yield (117.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.88 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 8.6 Hz, 2H), 3.79 (d, J = 11.2 Hz, 6H), 3.61(d, J = 22.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):δ190.8 (d, J = 6.0 Hz), 135.1 (d, J = 2.2 Hz), 132.1, 130.5, 129.3, 53.3 (d, J = 6.5 Hz), 37.6 (d, J = 130.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.30; MS (ESI-TOF) *m/z*: $(M+Na)^+$Calcd for $C_{10}H_{12}BrO_4PNa$ 328.9, found 328.9.

*Dimethyl (2-oxo-2-(3-(trifluoromethyl)phenyl)ethyl)phosphonate (**5h**)*

Colorless liquid, 60% yield (117.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ8.27 (s, 1H), 8.21 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 3.80 (d, J = 11.3 Hz, 6H), 3.68 (d, J = 22.8 Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$): δ190.5 (d, J = 6.7 Hz), 136.8 (d, J = 2.1 Hz), 132.2, 131.4 (q, J = 33.0 Hz), 130.1 (q, J = 3.5 Hz), 129.4, 125.8 (q, J = 3.8 Hz), 123.6 (q, J = 270.9 Hz), 53.2 (d, J = 6.6 Hz), 37.8 (d, J = 130.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ21.80; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{11}H_{13}F_3O_4P$ 297.0504, found 297.0509.

*Dimethyl (2-(4-cyanophenyl)-2-oxoethyl)phosphonate (**5i**)*

Colorless liquid, 59% yield (149.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 3.78 (d, J = 13.5 Hz, 6H), 3.66 (d, J = 22.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):δ190.1 (d, J = 6.7 Hz), 138.7 (d, J = 1.9 Hz), 132.1, 128.9, 117.3, 116.5, 52.9 (d, J = 6.6 Hz), 37.5 (d, J = 130.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.41; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{11}H_{13}NO_4P$ 254.0582, found 254.0583.

*Dimethyl (2-(4-nitrophenyl)-2-oxoethyl)phosphonate (**5j**)*

Yellow liquid, 50 % yield (136.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (d, J = 8.7 Hz, 2H), 8.20 (d, J = 8.8 Hz, 2H), 3.81 (d, J = 11.3 Hz, 6H), 3.71 (d, J = 22.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$):δ 190.4 (d, J = 6.8 Hz), 150.6, 140.6 (d, J = 2.0 Hz), 130.1, 123.9, 53.4 (d, J = 6.6 Hz), 38.1 (d, J = 129.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.30; HRMS (ESI-TOF) *m/z*: $(M+Na)^+$Calcd for $C_{10}H_{12}NNaO_6P$ 296.0300, found 296.0318.

*Dimethyl (2,2-diphenylvinyl)phosphonate (**5m**)*[20]

Colorless liquid; 75% yield (216.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.42–7.27 (m, 10H), 6.18 (d, J = 15.6 Hz, 1H), 3.50 (d, J = 11.1 Hz, 6H);^{13}C NMR (75 MHz, $CDCl_3$): δ160.8 (d, J = 6.4 Hz), 141.1 (d, J = 29.7 Hz), 138.7 (d, J = 7.6 Hz), 129.5, 128.7, 128.3,128.1, 127.9, 127.0, 125.7, 114.8, 112.2, 52.1 (d, J = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$):δ19.47; HRMS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{16}H_{18}O_3P$ 289.0994, found 289.1003.

*(E)-Dimethyl styrylphosphonate (**5o**)*[21]

Colorless liquid, 64% yield (135.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ7.54–7.62 (m, 1H), 7.49–7.53 (m, 2H), 7.38–7.43 (m, 3H), 6.19–6.29 (m, 1H), 3.79 (d, J = 11.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$):δ149.7 (d, J = 6.7 Hz), 134.6 (d, J = 23.3 Hz), 130.4, 128.9, 127.8, 112.3 (d, J = 191.3 Hz), 52.5 (d, J = 5.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$):δ22.35; MS (ESI-TOF) *m/z*: $(M+H)^+$Calcd for $C_{10}H_{14}O_3P$ 213.0, found 213.0.

Supplementary data

Copies of the ^{1}H, ^{13}C and ^{31}P NMR spectra for compounds **3** and **5** are available.

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