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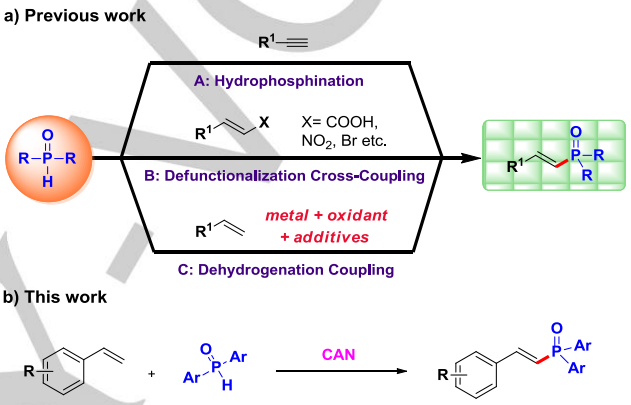
# Ceric(IV) Ammonium Nitrate Mediated Phosphorylation of Alkenes: Easy Access to (*E*)-Vinylphosphonates

Jian Shen, [a] Rui-Xiao Yu, [a] Yan Luo, [a] Li-Xuan Zhu, [a] Yue Zhang, [a] Xue Wang, [a] Bo Xiao, [a] Jian-Bo Cheng, [a] Bin Yang,*[a] and Gui-Zhi Li*[a]

**Abstract:** An inexpensive Ceric(IV) ammonium nitrate mediated phosphorylation of alkenes has been developed. Without adding expensive metals and other additives, various (*E*)-alkenylphosphine oxides are obtained through an easy route in a one-pot manner. Preliminary mechanistic studies reveal that a spontaneous elimination process is involved in this process.

## Introduction

Alkenylphosphorus compounds are of widespread interest in organic chemistry. This is due to their remarkable chemical, physical and biological properties which provide extensive applications in organic chemistry, [1] materials science [2] and biochemistry. [3] As a consequence, numerous efforts have been directed toward the development of simple and stereoselective methods to access this motif. This area has been dominated by three types of transition-metal catalyzed C($sp^2$)−P bond formation strategies: hydrophosphination of alkynes (Scheme 1, a-A), [4] defunctionalization cross-coupling of functionalized alkenes (Scheme 1, a-B) [5] and the dehydrogenation coupling of alkenes (Scheme 1, a-C). [6] In 1996, the Tanaka and Han group reported the pioneering hydrophosphination of alkynes catalyzed by Pd and Pt catalysts. [4a] Subsequently, some other transition metals catalysts were employed for this reaction. The 100% atom utilization makes this strategy highly economical. However, the use of precious metals and the problems of stereo- and regioselectivity control encourage further exploration in this area. Defunctionalization cross-coupling of functionalized alkenes is another attractive strategy for the synthesis of alkenylphosphorus compounds. Much progress has been made, such as the decarboxylative, denitration and dehalogenation cross-couplings. However, requirement of specifically functionalized precursors and the generation of stoichiometric wastes limit their development. Alkenes are common building blocks in organic chemistry that makes them easily accessible. In recent years, the dehydrogenation coupling reaction of alkenes and P(O)−H species has been developed as an efficient protocol for the synthesis of alkenylphosphorus compounds. [6a-6c] Although this strategy has a high atom efficiency, only a few progresses have been made and the problems associated with the use of expensive metals, a stoichiometric amount of oxidants and excess additive have encouraged researchers to expand simpler and more efficient methods.




**Scheme 1.** Synthesis of alkenylphosphorus compounds.

In recent years, P-radical involved C−H phosphorylations have become a powerful protocol for the construction of diversified C-P bonds.[7] In these works, Ag, Mn and Cu salts are the most commonly used initiators to produce a P(O)-radical. The unveiling of new strategies for C-P bond formation has dominated our interests. [8] Recently, we have developed the first example of a Ce(IV) initiated P(O)-radical difunctionalization of alkenes, which provides an alternative approach in P-radical chemistry. [8d] This success and our continued interest in Ce(IV) mediated C-P bond formations encouraged us to explore whether the alkenylphosphorus compounds could be formed under such a simple reaction system. To our delight, by using CAN only, vinylphosphonates can be generated with high selectivity (Scheme 1, b). Herein, we describe a new CAN-promoted phosphorylation of alkenes. In this process, without adding expensive metals and other additives, various (*E*)-alkenylphosphine oxides can be obtained in a one-pot manner.

## Results and Discussion

We commenced our study with the reaction of styrene **1a** and diphenylphosphine oxide **2a** in the presence of 2.0 equiv. of CAN in 1,4-dioxane (2.0 mL) at 40 °C under a nitrogen atmosphere for 18 h. Gratifyingly, we observed that the (*E*)-diphenyl(styryl)phosphine oxide **3a** was obtained, but in only 8 % yield (Table 1, entry 1). In order to improve the yield, we screened a variety of reaction conditions at the early stage，

[a] College of Chemistry and Chemical Engineering, Yantai University, Yantai 264005, P. R. China.
E-mail: yangbin_hy@ytu.edu.cn
liguizhi@ytu.edu.cn
http://www.chem.ytu.edu.cn/info/1100/2006.htm
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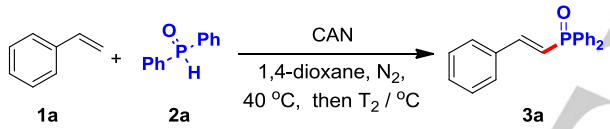
such as different solvents, reaction temperature, ratio of two starting materials, loading of CAN, various additives (see the SI for more details), however, no satisfactory results were achieved. It delights us that, by stirring the reaction initially at 40 °C for 10 h, and then turned reaction temperature to 80 °C and stirred at this temperature for another 12 h, a respectable yield of the target product **3a** (64 %) was gained (Table 1, entry 2). Encouraged by this promising result, we further optimized the reaction conditions. The reaction temperature screening shows that increasing $T_2$ from 80 °C to 90 °C could result in a good yield of 73 %, a further increase in temperature did not increase the yield (Table 1, entries 3-4). The amount of CAN was investigated, but it was found that neither a reduction nor an increase resulted in higher yields (Table 1, entries 5-6). Next, the ratio of styrene **1a** and diphenylphosphine oxide **2a** was surveyed, and the results show that the ratio of 2.5: 1 was still the best choice (Table 1, entries 7-8). The reaction concentration had a notable effect on the yield. Whereas a lower concentration lead to a lower yield (Table 1, entry 9), it is pleasure to find that increasing the concentration could result in a higher yield (Table 1, entry 10). When the concentration was increased further, the yield was reduced (Table 1, entry 11). Avoiding the initial heating at 40 °C, the reaction stirred at 90 °C for 22 h, we only obtained a small amount of product (Table 1, entry 12). For achieving higher yield at one temperature, we also did many reaction conditions screening (see the SI for details), but no good yield was obtained. After the screening, the optimal reaction conditions were established as listed in Table 1, entry 10: 2.5 equiv of **1a** and 1.0 equiv of **2a** with 2.0 equiv of CAN in the presence of 1.0 mL of 1,4-dioxane under $N_2$ atmosphere, stirred at 40 °C for 10 h, then stirred at 90 °C for 12 h.

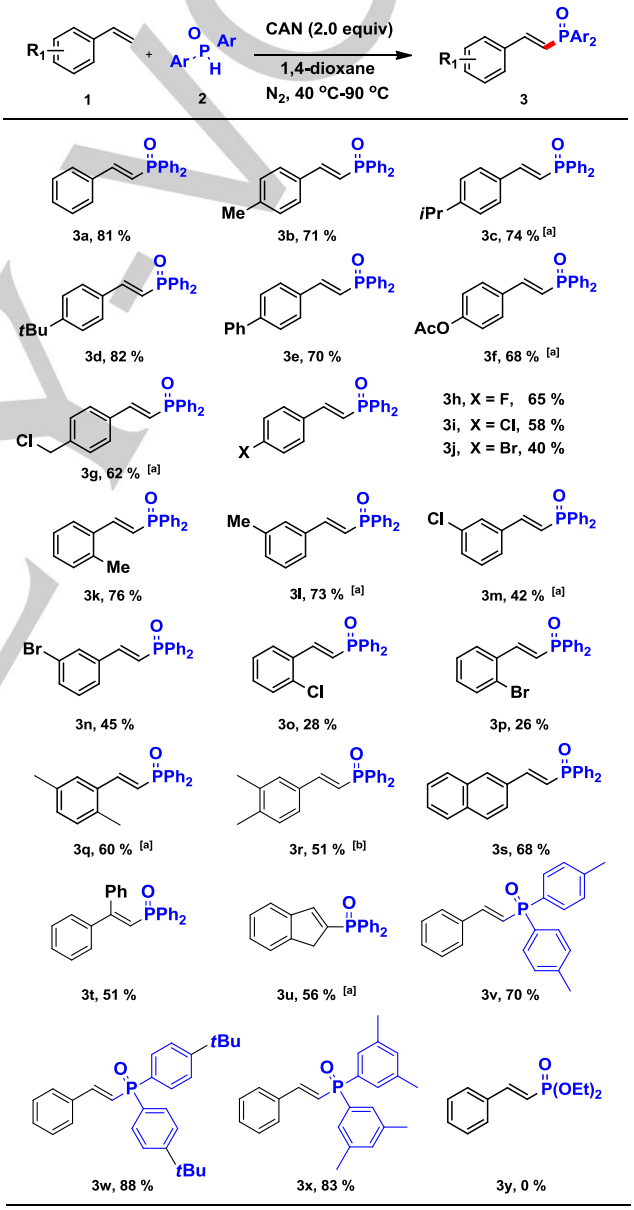
With the optimized reaction conditions in hand, the substrate scope was explored, and the results are summarized in Scheme 2. A variety of (*E*)-alkenylphosphine oxides were obtained with

**Table 1.** Selected reaction condition optimizations [a,b]



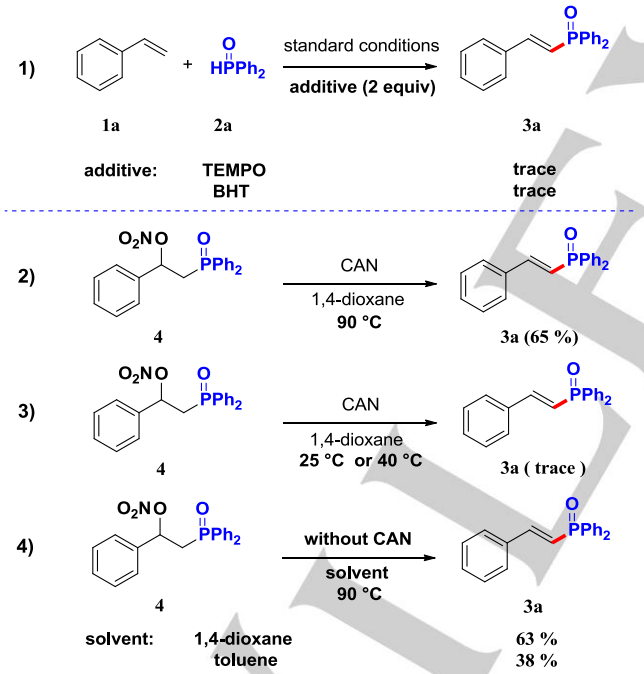

| Entry | CAN ( equiv ) | 1a / 2a | $T_2$ / °C | Yield (%) |
|---|---|---|---|---|
| 1 | 2.0 | 2.5 : 1.0 | 40 | 8 |
| 2 | 2.0 | 2.5 : 1.0 | 80 | 64 |
| 3 | 2.0 | 2.5 : 1.0 | 90 | 73 |
| 4 | 2.0 | 2.5 : 1.0 | 100 | 72 |
| 5 | 1.5 | 2.5 : 1.0 | 90 | 68 |
| 6 | 2.5 | 2.5 : 1.0 | 90 | 71 |
| 7 | 2.0 | 2.0 : 1.0 | 90 | 59 |
| 8 | 2.0 | 3.0 : 1.0 | 90 | 67 |
| 9[c] | 2.0 | 2.5 : 1.0 | 90 | 66 |
| **10[d]** | **2.0** | **2.5 : 1.0** | **90** | **81** |
| 11[e] | 2.0 | 2.5 : 1.0 | 90 | 62 |
| 12[f] | 2.0 | 2.5 : 1.0 | 90 | 43 |

[a] Reaction condition: **1a** (0.5 mmol), **2a** (0.2 mmol), $(NH_4)_2Ce(NO_3)_6$ (0.4 mmol), 1,4-dioxane (2.0 mL), $N_2$, stirred at 40 °C for 10 h, then stirred at 90 °C for 12 h; [b] Isolated yield; [c] 1,4-dioxane (3.0 mL); [d] 1,4-dioxane (1.0 mL); [e] 1,4-dioxane (0.5 mL); [f] Instead of stirring at 40 °C for 10 h, stirred at 90 °C for 22 h directly.



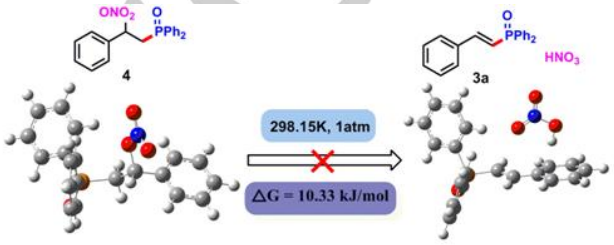

**Scheme 2.** Substrate scope. Unless otherwise specified, all reactions were carried out with **1** (0.5 mmol), **2** (0.2 mmol), CAN (0.4 mmol), 1,4-dioxane (1.0 mL), $N_2$, stirred at 40 °C for 10 h, then stirred at 90 °C for 12 h, yields are given for isolated products. [a] 1,4-dioxane (2.0 mL); [b] CAN (0.3 mmol).

high stereoselectivity. Substituted styrenes were initially examined. When different substituents were located on the *para*-position of the aryl ring, such as various alkyl or aryl groups (**3b–3e**), ester(**3f**), chloromethyl (**3g**), halogens (**3h-3j**), the corresponding products were obtained in moderate to good yields. This shows that the electronic effect had an obvious effect on the yield. Higher yields obtained with electron-donating groups (**3b-3f**) than with electron-withdrawing groups (**3g-3j**). Remarkably, both the *ortho*- and *meta*- substituted substrates could afford the corresponding products (**3k-3p**). It is notable that when a halogen is located in the *ortho*-position (**3o-3p**), the lowest yields were observed. The electronic and steric hindrance effects might both be responsible for this result. Moreover, multi-substituted substrates (**3q-3r**) and other aromatic ring (**3s**), reacted smoothly and were converted into the corresponding products with moderate yields. It is noteworthy that the α-phenyl substituted styrene (**3t**) and indene (**3u**) could also be tolerated in this reaction. Finally, we investigated other P(O)-H reagents. To our delight, several substituted diphenylphosphine oxides provided the corresponding products **3v, 3w, 3x** in good yields. Nevertheless, this process was not applicable to phosphites, where the phosphinoylation-nitrooxylation product was detected instead of the vinylphosphonate (**3y**).



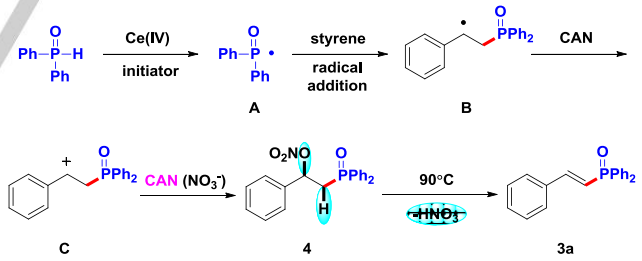

**Scheme 3.** Control experiments.

In order to clarify the reaction mechanism, a series of control experiments were conducted to explore this transformation (Scheme 3). As shown, the reaction was suppressed dramatically by the addition of 2.0 equivalents of 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) or 2,6-di-*tert*-butyl-*p*-cresol (BHT) under the standard conditions (Scheme 3, Eq 1), indicating that a radial pathway might be involved in this process. According to our previous findings, [8d] we predicted that product **3a** may be converted from the nitrate ester **4**. In order to verify this inference, we employed compound **4** as the substrate to conduct this reaction at 90 °C for 12h. As we expected, **3a** was obtained with a 65 % yield (Scheme 3, Eq 2). However, when the reaction temperature was reduced to 40 °C or 25 °C, **3a** was hardly observed (Scheme 3, Eq 3). To our surprise, in the absence of CAN, **4** can still be converted into **3a** (Scheme 3, Eq 4). These results suggest that the reaction temperature plays a decisive role in the generation of **3a** and the transformation from **4** to **3a** is a spontaneous process at high temperature.




**Scheme 4.** Computered gibbs free energy.

Moreover, in order to increase our comprehension of this process, a Gibbs free energy calculation was carried out to investigate the key step in the generation of **3a** (Scheme 4). The result shows that **4** can't be converted into **3a** at low temperature environment (298.15 K, 1 atm), where the ΔG is calculated as 10.33 kJ/mol.




**Scheme 5.** Plausible mechanistic pathway.

Based on the above preliminary mechanistic studies and previous reports, we propose a plausible pathway for this phosphorylation reaction of alkenes (Scheme 5). Initially, the phosphorus radical **A** is generated from diphenylphosphine oxide by Ce(IV). Then, following radical addition and single electron oxidation steps, the carbon-cation intermediate **C** is formed. Subsequently, intermediate **4** is produced by the nucleophilic attack of a nitrate ion, which undergoes a spontaneous elimination reaction at 90 °C with elimination of $HNO_3$ to form the desired vinylphosphonate product **3a**.

## Conclusions

In summary, we have developed a concise and efficient protocol of ceric(IV) ammonium nitrate promoted phosphorylation of alkenes in a one-pot manner, which provides an easy approach to various (*E*)-alkenylphosphine oxides. This reaction proceeds under simple reaction conditions without adding expensive metals or other additives. It exhibits high atom economy and is environmentally friendly. Preliminary mechanistic studies show that a spontaneous elimination process is involved in this transformation. Further exploration of the reaction mechanism is ongoing in our laboratory.

## Experimental Section

**General methods**:$^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker advance Ⅲ 400 spectrometer in $CDCl_3$ with TMS as internal standard. $^{31}$P NMR and $^{19}$F NMR spectra were recorded on the same instrument. Mass spectra were mearsured using Esquire6000. High-resolution mass spectrometry (HRMS) spectra were obtained on a Bruker micro TOF-Q II instrument. Melting points were measured on a WRS-1C digital melting point apparatus and are uncorrected. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM). All the computational calculations are carried out with the GAUSSIAN 09 program. [9] The optimized geometries and harmonic frequencies of the structure **4** and **3a** are calculated using the B3LYP method with 6-31+G(d) basis set.

**Typical Procedure for the Synthesis of Compounds 3:** To a Schlenk tube was added diphenylphosphine oxide **2a** (0.2 mmol) and $(NH_4)_2Ce(NO_3)_6$ (0.4 mmol) before being charged with nitrogen three times. Then, anhydrous 1,4-dioxane (1.0 mL) and styrene **1a** (0.5 mmol) were added via syringe. The mixture was allowed to stir at 40 $^{o}$C in an oil bath for 10 h, then the temperature was raised to 90 $^{o}$C, stirred at this temperature for another 12 h. On the completion of the reaction, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to afford the product (*E*)-diphenyl(styryl)phosphine oxide **3a**.

**(*E*)-diphenyl(styryl)phosphine oxide (3a):** White solid, m.p. 162-163 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.79-7.74 (m, 4H), 7.57-7.46 (m, 9H), 7.40-7.37 (m, 3H), 6.85 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.5 (d, $J_{C\text{-}P}$ = 3.5 Hz), 135.1 (d, $J_{C\text{-}P}$ = 17.6 Hz), 133.0 (d, $J_{C\text{-}P}$ = 105.4 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.1, 128.8, 128.6 (d, $J_{C\text{-}P}$ = 12.2 Hz), 127.7, 119.2 (d, $J_{C\text{-}P}$ = 104.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.52. HRMS(ESI) calc. for $C_{20}H_{18}OP$ $(M+H)^+$: 305.1095, found 305.1100.

**(*E*)-(4-methylstyryl)diphenylphosphine oxide (3b):**[5n] Brown solid, m.p. 191-192 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.56-7.41 (m, 9H), 7.18 (d, $J$ = 8.0 Hz, 1H), 6.78 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.4 Hz, 1H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.5(d, $J_{C\text{-}P}$ = 3.7 Hz), 140.4, 133.0 (d, $J_{C\text{-}P}$ = 105.3 Hz), 132.3, 131.8 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.5, 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.7, 117.7 (d, $J_{C\text{-}P}$ = 104.7 Hz), 21.4. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.74; MS (ESI): 637.5 $(2M+H)^+$.

**(*E*)-(4-isopropylstyryl)diphenylphosphine oxide (3c):** White solid, m.p. 152-153 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 4H), 7.57-7.41 (m, 9H), 7.26-7.23 (m, 2H), 6.77 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.5 Hz, 1H), 7.97-7.87 (m, 1H), 1.25 (d, $J$ = 7.0 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 151.6, 148.1 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.7 (d, $J_{C\text{-}P}$ = 4.4 Hz), 132.1 (d, $J_{C\text{-}P}$ = 1.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 83.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.1 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.1 Hz), 128.0, 127.0, 117.0 (d, $J_{C\text{-}P}$ = 105.6 Hz), 34.0, 23.7. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 26.91. HRMS(ESI) calc. for $C_{23}H_{24}OP$ $(M+H)^+$: 347.1559, found 347.1552.

**(*E*)-(4-(tert-butyl)styryl)diphenylphosphine oxide (3d)** [6b]**:** White solid, m.p. 158-159 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.55-7.40 (m, 11H), 6.80 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.4 Hz, 1H), 1.32 (s, 9H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 153.6, 147.4 (d, $J_{C\text{-}P}$ = 3.5 Hz), 133.1 (d, $J_{C\text{-}P}$ = 105.3 Hz), 132.4 (d, $J_{C\text{-}P}$ = 17.9 Hz), 131.8, 131.4 (d, $J_{C\text{-}P}$ = 9.8 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.0 Hz), 127.5, 125.8, 118.1 (d, $J_{C\text{-}P}$ = 104.6 Hz), 34.8, 31.1. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.82. MS (ESI) : 721.6 $(2M+H)^+$.

**(*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)diphenylphosphine oxide (3e):**[5n] White solid, m.p. 203-204 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.81-7.77 (m, 4H), 7.64-7.35 (m, 16H), 6.89 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.3 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.0 (d, $J_{C\text{-}P}$ = 3.5 Hz), 142.8, 140.0, 134.0 (d, $J_{C\text{-}P}$ = 18.0 Hz), 132.9 (d, $J_{C\text{-}P}$ = 105.3 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.8, 128.6 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.2, 127.7, 127.4, 127.0, 119.0 (d, $J_{C\text{-}P}$ = 104.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.61. MS (ESI) : 761.4 $(2M+H)^+$.

**(*E*)-4-(2-(diphenylphosphoryl)vinyl)phenyl acetate (3f):**[5n] Yellow solid, m.p. 157-158 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 4H), 7.56-7.44 (m, 9H), 7.11 (d, $J$ = 8.6 Hz, 2H), 6.79 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.2 Hz, 1H), 2.30 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.1, 151.9, 146.4, 133.0 (d, $J_{C\text{-}P}$ = 31.5 Hz), 132.4 (d, $J_{C\text{-}P}$ = 55.4 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.9, 128.6 (d, $J_{C\text{-}P}$ = 12.1 Hz), 122.0, 119.3 (d, $J_{C\text{-}P}$ = 103.7 Hz), 21.1. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.65. MS (ESI) : 725.5 $(2M+H)^+$.

**(*E*)-(4-(chloromethyl)styryl)diphenylphosphine oxide (3g):** Yellow solid, m.p. 159-160 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.56-7.46 (m, 9H), 7.69 (d, $J$ = 8.1 Hz, 2H), 6.86 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.2 Hz, 1H), 4.57 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 146.6 (d, $J_{C\text{-}P}$ = 3.5 Hz), 139.3, 135.1 (d, $J_{C\text{-}P}$ = 16.8 Hz), 132.6 (d, $J_{C\text{-}P}$ = 105.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.3 (d, $J_{C\text{-}P}$ = 10.0 Hz), 129.0, 128.6 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.0, 119.9 (d, $J_{C\text{-}P}$ = 103.3 Hz), 45.6. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.36. HRMS(ESI) calc. for $C_{21}H_{19}ClOP$ $(M+H)^+$: 353.0857, found 353.0849.

**(*E*)-(4-fluorostyryl)diphenylphosphine oxide (3h):** [5n] Yellow solid, m.p. 164-165 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.56-7.43 (m, 9H), 7.06 (t, $J$ = 8.6 Hz, 2H), 6.76 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.1 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 163.7(d, $J_{C\text{-}F}$ = 249.2 Hz), 146.2 (d, $J_{C\text{-}F}$ = 3.4 Hz), 132.9 (d, $J_{C\text{-}P}$ = 105.5 Hz), 131.9, 131.3 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.6 (d, $J_{C\text{-}P}$ = 8.3 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.1 Hz), 119.0 (d, $J_{C\text{-}P}$ = 103.1 Hz), 116.0, 115.8. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.32; $^{19}$F NMR (376 MHz, $CDCl_3$) δ: -109.97; MS (ESI) : 645.3 $(2M+H)^+$.

**(*E*)-(4-chlorostyryl)diphenylphosphine oxide (3i):** [5n] White solid, m.p. 179-180 $^{o}$C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.57-7.44 (m, 9H), 7.34 (d, $J$ = 8.0 Hz, 2H), 6.83 (t, $J$ = 20.4 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 146.0, 136.0, 133.6 (d, $J_{C\text{-}P}$ = 17.8 Hz), 132.7 (d, $J_{C\text{-}P}$ = 105.6 Hz), 131.9, 131.3 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.0 (d, $J_{C\text{-}P}$ = 14.0 Hz), 128.7, 128.6, 120.0 (d, $J_{C\text{-}P}$ = 103.3 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.18. MS (ESI): 677.2 $(2M+H)^+$.

**(*E*)-(4-bromostyryl)diphenylphosphine oxide (3j):** White solid, m.p. 186-187 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 4H), 7.56-7.37 (m, 11H), 6.85 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 146.1 (d, $J_{C-F}$ = 3.5 Hz), 134.0 (d, $J_{C-F}$ = 17.8 Hz), 132.7 (d, $J_{C-F}$ = 105.6 Hz), 132.1, 132.0 (d, $J_{C-F}$ = 2.1 Hz), 131.4 (d, $J_{C-P}$ = 10.0 Hz), 129.2, 128.7 (d, $J_{C-P}$ = 12.1 Hz), 124.3, 120.2 (d, $J_{C-P}$ = 102.7 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.13. HRMS(ESI) calc. for $C_{20}H_{17}BrOP$ (M+H)$^+$: 383.0195, found 383.0187.

**(*E*)-(2-methylstyryl)diphenylphosphine oxide (3k):**[5n] Yellow solid, m.p. 160-161 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.81-7.72 (m, 5H), 7.59-7.45 (m, 7H), 7.27-7.17 (m, 3H), 6.78 (dd, $J_1$ = 17.3 Hz, $J_2$ = 23.2 Hz, 1H), 2.36 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 145.3 (d, $J_{C-P}$ = 3.6 Hz), 137.1, 134.1 (d, $J_{C-P}$ = 17.3 Hz), 132.9 (d, $J_{C-P}$ = 105.0 Hz), 131.8 (d, $J_{C-P}$ = 2.2 Hz), 131.3 (d, $J_{C-P}$ = 9.9 Hz), 130.7, 129.7, 128.5 (d, $J_{C-P}$ = 11.9 Hz), 126.2, 126.0, 120.4 (d, $J_{C-P}$ = 103.0 Hz), 19.6. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.61. MS (ESI) : 637.6 $(2M+H)^+$.

**(*E*)-(3-methylstyryl)diphenylphosphine oxide (3l):** Yellow solid, m.p. 126-127 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.55-7.45 (m, 7H), 7.33-7.24 (m, 3H), 7.18 (d, $J$ = 7.4 Hz, 1H), 6.82 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.4 Hz, 1H), 2.35 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.7(d, $J_{C-P}$ = 3.4 Hz), 138.5, 135.0 (d, $J_{C-P}$ = 17.8 Hz), 133.0 (d, $J_{C-P}$ = 105.0 Hz), 131.8 (d, $J_{C-P}$ = 2.0 Hz), 131.3 (d, $J_{C-P}$ = 10.0 Hz), 130.9, 128.7, 128.5 (d, $J_{C-P}$ = 12.0 Hz), 128.3, 125.0, 118.9 (d, $J_{C-P}$ = 104.2 Hz), 21.2. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.70. HRMS(ESI) calc. for $C_{21}H_{20}OP$ (M+H)$^+$: 319.1246, found 319.1240.

**(*E*)-(3-chlorostyryl)diphenylphosphine oxide (3m):** Yellow solid, m.p. 151-152 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.56-7.42 (m, 8H), 7.38-7.27 (m, 3H), 6.88 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 145.7 (d, $J_{C-P}$ = 3.7 Hz), 136.8 (d, $J_{C-P}$ = 18.1 Hz), 134.7，132.5 (d, $J_{C-P}$ = 105.6 Hz), 131.9 (d, $J_{C-P}$ = 2.1 Hz), 131.2 (d, $J_{C-P}$ = 9.9 Hz), 129.9 (d, $J_{C-P}$ = 20.0 Hz), 128.6 (d, $J_{C-P}$ = 12.1 Hz), 128.6 (d, $J_{C-P}$ = 12.1 Hz), 127.2, 126.1, 121.1 (d, $J_{C-P}$ = 102.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 23.91. HRMS(ESI) calc. for $C_{20}H_{17}ClOP$ (M+H)$^+$: 339.0700, found 339.0699.

**(*E*)-(3-bromostyryl)diphenylphosphine oxide (3n):** White solid, m.p. 164-165 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 4H), 7.67 (s, 1H), 7.57-7.40 (m, 9H), 7.26 (d, $J$ = 8.6 Hz, 1H), 6.86 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 145.8 (d, $J_{C-P}$ = 3.6 Hz), 137.2 (d, $J_{C-P}$ = 18.0 Hz), 133.1, 132.9, 132.1, 131.4 (d, $J_{C-P}$ = 10.0 Hz), 130.4, 130.2, 128.7 (d, $J_{C-P}$ = 10.2 Hz), 126.7, 123.0, 121.2 (d, $J_{C-P}$ = 102.0 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.08. HRMS(ESI) calc. for $C_{20}H_{17}BrOP$ (M+H)$^+$: 383.0195, found 383.0208.

**(*E*)-(2-chlorostyryl)diphenylphosphine oxide (3o):** Brown solid, m.p. 160-161 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.83-7.74 (m, 5H), 7.65-7.63 (m, 1H), 7.57-7.47 (m, 6H), 7.40-7.38 (m, 1H), 7.31-7.27 (m, 2H), 6.88 (dd, $J_1$ = 17.4 Hz, $J_2$ = 20.7 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 143.6 (d, $J_{C-P}$ = 5.3 Hz), 143.5, 133.5 (d, $J_{C-P}$ = 18.2 Hz), 133.0, 132.0 (d, $J_{C-P}$ = 2.2 Hz), 131.5 (d, $J_{C-P}$ = 9.8 Hz), 130.8, 130.1, 128.6 (d, $J_{C-P}$ = 12.1 Hz), 127.7, 127.0, 123.0 (d, $J_{C-P}$ = 102.3 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 25.33. HRMS(ESI) calc. for $C_{20}H_{17}ClOP$ (M+H)$^+$: 339.0700, found 339.0705.

**(*E*)-(2-bromostyryl)diphenylphosphine oxide (3p):** Yellow solid, m.p. 160-161 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.81-7.73 (m, 4H), 7.69-7.47 (m, 9H), 7.34-7.30 (m, 1H), 7.23-7.19 (m, 1H), 6.82 (dd, $J_1$ = 17.4 Hz, $J_2$ = 20.0 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 146.3 (d, $J_{C-P}$ = 5.6 Hz), 135.2 (d, $J_{C-P}$ = 20.0 Hz), 133.3, 132.7, 132.0 (d, $J_{C-P}$ = 2.7 Hz), 131.5 (d, $J_{C-P}$ = 9.8 Hz), 131.0, 128.6 (d, $J_{C-P}$ = 12.0 Hz), 127.8, 127.7, 124.8, 123.1 (d, $J_{C-P}$ = 102.2 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 25.22. HRMS(ESI) calc. for $C_{20}H_{17}BrOP$ (M+H)$^+$: 383.0195, found 383.0198.

**(*E*)-(2,5-dimethylstyryl)diphenylphosphine oxide (3q):** White solid, m.p. 212-213 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.81-7.71 (m, 5H), 7.54-7.45 (m, 6H), 7.40 (s, 1H), 7.06 (s, 2H), 6.77 (dd, $J_1$ = 17.3 Hz, $J_2$ = 23.3 Hz, 1H), 2.31 (d, $J$ = 4.2 Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 145.4 (d, $J_{C-P}$ = 3.9 Hz), 135.5, 134.0, 133.7 (d, $J_{C-P}$ = 17.0 Hz), 133.0 (d, $J_{C-P}$ = 104.9 Hz), 131.7 (d, $J_{C-P}$ = 2.1 Hz), 131.2 (d, $J_{C-P}$ = 9.8 Hz), 130.5 (d, $J_{C-P}$ = 1.9 Hz), 128.5, 128.4, 126.4, 119.9 (d, $J_{C-P}$ = 103.4 Hz), 20.8, 19.0. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.63. HRMS(ESI) calc. for $C_{22}H_{22}OP$ (M+H)$^+$: 333.1403, found 333.1399.

**(*E*)-(3,4-dimethylstyryl)diphenylphosphine oxide (3r):** White solid, m.p. 198-199 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 4H), 7.54-7.43 (m, 7H), 7.29-7.25 (m, 2H), 7.13 (d, $J_1$ = 7.8 Hz, 1H), 6.77 (dd, $J_1$ = 17.5 Hz, $J_2$ = 22.4 Hz, 1H), 2.26 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.7 (d, $J_{C-P}$ = 3.7 Hz), 139.1, 137.0, 133.6, 132.8 (d, $J_{C-P}$ = 18.1 Hz), 132.6, 131.7 (d, $J_{C-P}$ = 2.6 Hz), 131.3 (d, $J_{C-P}$ = 9.8 Hz), 130.0, 128.8, 128.5 (d, $J_{C-P}$ = 12.0 Hz), 117.5 (d, $J_{C-P}$ = 104.9 Hz), 19.7. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.85. HRMS(ESI) calc. for $C_{22}H_{22}OP$ (M+H)$^+$: 333.1403, found 333.1407.

**(*E*)-(2-(naphthalen-2-yl)vinyl)diphenylphosphine oxide (3s):**[5n] Yellow solid, m.p. 222-223 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.83-7.76 (m, 7H), 7.70-7.62 (m, 2H), 7.57-7.49 (m, 8H), 6.96 (dd, $J_1$ = 17.5 Hz, $J_2$ = 21.8 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.5 (d, $J_{C-P}$ = 3.5 Hz), 134.0, 133.2, 132.9 (d, $J_{C-P}$ = 106.7 Hz), 132.6, 131.8, 131.3 (d, $J_{C-P}$ = 9.8Hz), 129.3, 128.6, 128.5, 128.4, 127.7, 127.1, 126.6, 123.3, 119.4 (d, $J_{C-P}$ = 103.9 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.65. MS (ESI) : 709.5 $(2M+H)^+$.

**(2,2-diphenylvinyl)diphenylphosphine oxide (3t):** White solid, m.p. 171-172 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.70-7.66 (m, 4H), 7.39-7.29 (m, 11H), 7.22 (d, $J$ = 7.8 Hz, 2H), 7.15-7.06 (m, 3H), 6.78 (d, $J$ = 18.2 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 162.0, 141.9 (d, $J_{C-P}$ = 16.1 Hz), 138.0 (d, $J_{C-P}$ = 6.7 Hz), 134.8, 133.8, 131.0 (d, $J_{C-P}$ = 2.6 Hz), 130.8 (d, $J_{C-P}$ = 9.5 Hz), 130.3, 129.5, 128.6, 128.3, 128.3 (d, $J_{C-P}$ = 3.6 Hz), 128.2, 127.5, 120.5 (d, $J_{C-P}$ = 103.3 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 18.74. HRMS(ESI) calc. for $C_{26}H_{22}OP$ (M+H)$^+$: 381.1403, found 381.1397.

**(1H-inden-2-yl)diphenylphosphine oxide (3u):** Brown oil. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.77-7.72 (m, 4H), 7.58-7.45 (m, 8H), 7.34-7.26 (m, 3H), 3.69 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 146.0 (d, $J_{C-P}$ = 9.3 Hz), 145.8 (d, $J_{C-P}$ = 11.3 Hz), 142.7 (d, $J_{C-P}$ = 16.1 Hz), 139.0 (d, $J_{C-P}$ = 108.9 Hz), 132.7, 132.0 (d, $J_{C-P}$ = 2.6 Hz), 131.6 (d, $J_{C-P}$ = 10.0 Hz), 128.6 (d, $J_{C-P}$ = 12.3 Hz), 127.2, 127.0, 124.2, 122.8, 40.3 (d, $J_{C-P}$ = 11.8 Hz). $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.24. HRMS(ESI) calc. for $C_{21}H_{18}OP$ (M+H)$^+$: 317.1090, found 317.1085.

**(*E*)-styryldi-*p*-tolylphosphine oxide (3v):** Yellow solid, m.p. 162-163 °C. m.p. 150-151 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.67 (s, 4H), 7.53 (d, $J$ = 4.3 Hz, 3H), 7.38 (d, $J$ = 4.6 Hz, 3H), 7.29 (d, $J$ = 7.3 Hz, 4H), 6.90-6.81 (m, 1H), 2.42 (s, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 147.1, 142.3 (d, $J_{C-P}$ = 2.4 Hz), 135.2 (d, $J_{C-P}$ = 17.8 Hz), 131.4 (d, $J_{C-P}$ = 10.3 Hz), 130.2, 129.9, 139.3 (d, $J_{C-P}$ = 12.5 Hz), 128.7, 127.7, 119.6 (d, $J_{C-P}$ = 102.6 Hz), 21.6. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.92. HRMS(ESI) calc. for $C_{22}H_{22}OP$ (M+H)$^+$: 333.1403, found 333.1391.

**(*E*)-bis(4-(tert-butyl)phenyl)(styryl)phosphine oxide (3w):** Yellow solid, m.p. 243-244 °C. $^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.71-7.66 (m, 4H), 7.55-7.46 (m, 7H), 7.36 (d, $J$ = 5.8 Hz, 3H), 6.83 (dd, $J_1$ = 17.4 Hz, $J_2$ = 22.2 Hz, 1H), 1.32 (s, 18H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 155.2 (d, $J_{C-P}$ = 2.5

Hz), 146.8 (d, $J_{C-P}$ = 3.3 Hz), 135.2 (d, $J_{C-P}$ = 17.6 Hz), 131.2 (d, $J_{C-P}$ = 10.1 Hz), 129.8, 129.7 (d, $J_{C-P}$ = 107.6 Hz), 128.7, 127.7, 125.5 (d, $J_{C-P}$ = 12.2 Hz), 119.9 (d, $J_{C-P}$ = 103.7 Hz), 34.9, 31.1. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.17. HRMS(ESI) calc. for $C_{28}H_{34}OP$ $(M+H)^+$: 417.2342, found 417.2340.

**(*E*)-bis(3,5-dimethylphenyl)(styryl)phosphine oxide (3x):** Yellow solid, m.p. 158-159 °C. $^1$H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.55-7.46 (m, 3H), 7.38-7.35 (m, 7H), 7.15 (s, 2H), 6.83 (dd, $J_1$ = 17.5 Hz, $J_2$ = 22.5 Hz, 1H), 2.34 (s, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 146.9 (d, $J_{C-P}$ = 3.4 Hz), 138.2 (d, $J_{C-P}$ = 12.7 Hz), 135.2 (d, $J_{C-P}$ = 17.4 Hz), 133.5 (d, $J_{C-P}$ = 2.7 Hz), 132.7 (d, $J_{C-P}$ = 104.5 Hz), 129.9, 128.8, 128.7, 127.7, 119.5 (d, $J_{C-P}$ = 103.0 Hz), 21.2. $^{31}$P NMR (162 MHz, $CDCl_3$): δ 24.95. HRMS(ESI) calc. for $C_{24}H_{26}OP$ $(M+H)^+$: 361.1716, found 361.1710.

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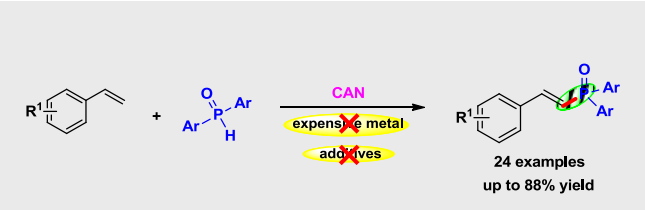


Without adding expensive metals and other additives, various (*E*)-alkenylphosphine oxides can be synthesized in a one-pot manner by using inexpensive Ceric(IV) ammonium nitrate under mild reaction conditions.

**One-Pot Reaction**

*J. Shen, R.-X. Yu, Y. Luo, L.-X. Zhu, Y. Zhang, X. Wang, B. Xiao, J.-B. Cheng, B. Yang*, G.-Z. Li**

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**Ceric(IV) Ammonium Nitrate Mediated Phosphorylation of Alkenes: Easy Access to (*E*)-Vinylphosphonates**