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Silver-catalyzed synthesis of 2-arylvinylphosphonates by cross-coupling of β-nitrostyrenes with *H*-phosphites

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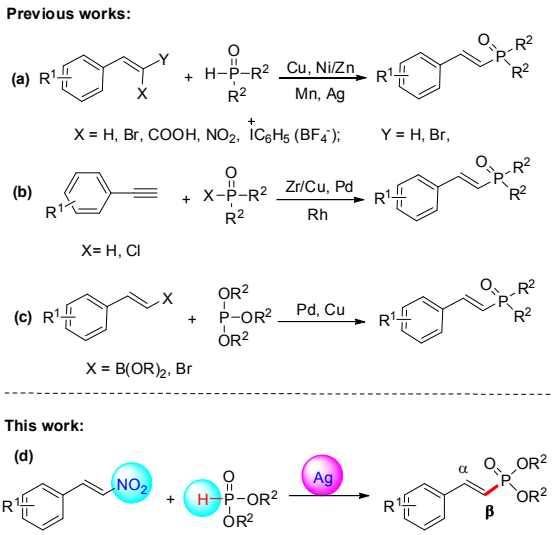
An efficient protocol for stereoselective synthesis of 2-arylvinylphosphonates has been developed via $AgNO_3$-catalyzed cross-coupling of β-nitrostyrenes with dialkyl *H*-phosphites under mild conditions. With losing nitro group of β-nitrostyrenes, the reaction proceeds smoothly and could provide the desired products with moderate to good yield.

Introduction

Vinylphosphonates are important molecules known for their interesting properties spanning across chemistry as well as biology.[1] They are suitable substrates for various name reactions such as Michael additions, cycloaddition, and Horner-Wadsworth-Emmons reactions.[2] They have been also extensively used in polymer sciences as additives or flame-retardants.[3] In medical chemistry, vinylphosphonates often exhibit interesting biological properties such as antiviral, antibacterial, anticancer implications.[4] For these reasons, the development of simple and stereoselective methods to prepare vinylphosphonates has become important in organic synthesis.

In recent years, a wide variety of transition metal catalyzed cross-coupling reactions for the construction of C–P bond have been developed.[5] As a significant motif in organic chemistry, the alkenyl C_{sp2}–P bond formation has attracted much attention. There are two main strategies applicable in forming the alkenyl C_{sp2}–P bond: the phosphorylation of alkynes or terminal alkynes, and functionalized alkenes. Dialkyl *H*-phosphites are coupled with functionalized alkenes including styrene, 2,2-dibromostyrenes, alkenyl acids, vinyliodonium tetrafluoroborates to form 2-arylvinylphosphonates using Cu as a catalyst.[6] Transition-metals such as Ni, and Ni/Zn-catalyzed reactions of alkenyl acids, 2,2-dibromostyrenes with dialkyl phosphites have been reported.[7] In 2015, Zou has described that Mn(III)-mediated alkenyl C(sp^2)-P bond formation from the reaction of 2-nitrostyrenes with dialkyl phosphites, and Tan found an efficient Ag-catalyzed reaction of styrenes with dialkyl phosphites using $K_2S_2O_8$ as the oxidant, and TEMPO as the additive[8] (**Scheme 1**, a). Transition metals such as Zr/Cu, Pd and Rh catalysts were employed for the reaction of terminal alkynes with Dialkyl *H*-phosphites and dialkyl chlorophosphates (**Scheme 1**, b).[9] It has also been reported that trialkyl phosphates react with 1-bromoalkenes and vinylboronate esters catalyzed by transition metal Pd, and Cu (**Scheme 1**, c).[10] Moreover, 2-arylvinylphosphonates are formed by the Mizoroki-Heck reaction of arylboronic acids with dialkyl vinylphosphonates catalyzed by $Pd(OAc)_2$, and via nucleophilic substitution of benzyl bromides with Bestmann-Ohira reagents.[11] Although these approaches are available for the synthesis of 2-arylvinylphosphonates, most of them suffer from several drawbacks such as lack of stereoselectivity (a mixture of E/Z products), the need to use a rather expensive catalyst, drastic conditions being not compatible with molecules containing sensitive functional groups. As a result, there is still a strong need for alternative methods that would allow the stereoselective synthesis of 2-arylvinylphosphonates from readily available starting materials and catalysts under mild reaction conditions.



Scheme 1 Strategies for synthesis of 2-arylvinylphosphonates

(*E*)-β-Nitrostyrenes are useful intermediates in organic synthesis and are important structural units that can be used

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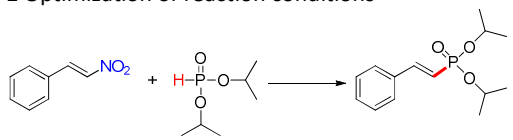
as starting material for many classes of compounds.[12] In general, the nitro group activates α- and/or β-position of a substrate, and in the reaction the nitro group is either remaining or leaving.[13] (*E*)-β-Nitrostyrenes are good radical acceptors and react with alkyl radicals from different sources to generate (*E*)-alkenes under a variety of conditions and the reaction mechanism appears to involve a free-radical addition-elimination reaction.[14] Although Zou has described that 2-arylvinylphosphonates could be synthsized by Mn(III)-catalyzed reaction of 2-nitrostyrenes with dialkyl phosphites,[8a] and Tan has found that Ag-catalyzed reaction of styrenes with dialkyl phosphites,[8b] these methodologies need use expensive and unstable catalysts, acid circumstance, strong oxidants, or with low yield. Drawing inspiration from recent studies[15] that dialkyl phosphites could be utilized as a phosphoryl radical precursor,[16] we wonder that 2-arylvinylphosphonates can be synthesized by cross-coupling of β-nitrostyrenes with dialkyl *H*-phosphites. Herein, we describe a new silver-catalyzed cross-coupling reaction between readily available β-nitrostyrenes with dialkyl *H*-phosphites, leading to 2-arylvinylphosphonates in moderate to excellent yields. Some notable features of this protocol are high efficiency, wide functional group tolerance, readily available and stable β-nitrostyrenes with dialkyl *H*-phosphites as starting materials, no oxidants and high stereoselectivity (**Scheme 1**, d).

Results and discussion

Our previous studies showed that the phosphoryl radicals could be easily generated from *H*-phosphites with a catalytic amount of silver salts.[16] Based on this achievement, the model reaction of (*E*)-β-nitrostyrenes (**1a**) and diisopropyl *H*-phosphite (**2a**) was carried out in the presence of $AgNO_3$ (0.1 eq) in CH_3CN at 90 ^oC for 20 min. Much to our delight, the desired product (**3a**) was indeed obtained, and the isolated yield was 56% (Table 1, entry 1). The *E* or *Z* stereochemistry of **3a** is easily established by the ^1H NMR analysis. Indeed, the report in the literature has shown that the chemistry shift of β-H proton is 6.10-6.30 ppm with a coupling constant 17.0 Hz typical of *trans* positioned protons, while that of *cis* isomer gives 5.60-5.80 ppm with a coupling constant 15.0 Hz.[9a] The β-proton of **3a** at δ_H=6.27 ppm appears as a triplet with a coupling constant, *J* = 17.6 Hz, which proves that configuration of **3a** is an *E* stereoisomer.

To achieve the optimal conditions, a variety of reaction conditions were employed. Initial screening of different solvents including H_2O, dioxane, CH_3OH, DMSO, DCE and THF were applied instead of CH_3CN. The result revealed that solvents such as H_2O and CH_3OH are not suitable for this reaction, and CH_3CN was clearly the best choice (**Table 1**, entries 1-7). The ratio of substrates (*E*)-β-nitrostyrenes and diisopropyl *H*-phosphite was investigated, and the ratio of 1 : 1.5 could provide the best result (**Table S1**, ESI). The screening of the amount of the catalyst $AgNO_3$ showed that a good yield (60%) of the product **3a** was obtained when 0.15 equiv of $AgNO_3$ was employed, and excessive or less amount of the catalyst caused decreased yield (**Table 1**, entries 1, 8-10). Furthermore, various reaction temperatures were investigated, and increasing the temperature from 40 to 100 ^oC could enhance the reaction efficacy, and a good yield of 56% could be obtained at 90 ^oC (**Table 1**, entries 1, 11-14). Based on these joyful results, various catalysts of silver salts such as AgOTf and Ag_2CO_3 were further investigated. It was found that they proved to be less effective compared with $AgNO_3$ (**Table 1**, entries 1, 15 and 16). In addition, various reaction times were also examined. The yield of **3a** dramatically increased if the reaction time was increased, 2.0 h was found to be appropriate choice and the yield was 78% (**Table 1**, entries 1, 17-20). In the absence of $AgNO_3$, the desired product **3a** was not produced, which indicated that $AgNO_3$ as a catalyst played an important role in this transformation (**Table 1**, entry 21).

Table 1 Optimization of reaction conditions[a]



1a 2a 3a

Entry	Oxidant (eq.)	Solvent	Temp (^oC)	Time (min)	Yield[b] (%)
1	$AgNO_3$ (0.1)	CH_3CN	90	20	56
2	$AgNO_3$ (0.1)	H_2O	90	20	<5
3	$AgNO_3$ (0.1)	Dioxane	90	20	0
4	$AgNO_3$ (0.1)	CH_3OH	90	20	40
5	$AgNO_3$ (0.1)	DMSO	90	20	<5
6	$AgNO_3$ (0.1)	DCE	90	20	54
7	$AgNO_3$ (0.1)	THF	90	20	30
8	$AgNO_3$ (0.05)	CH_3CN	90	20	45
9	$AgNO_3$ (0.15)	CH_3CN	90	20	60
10	$AgNO_3$ (0.2)	CH_3CN	90	20	55
11	$AgNO_3$ (0.15)	CH_3CN	40	20	trace
12	$AgNO_3$ (0.15)	CH_3CN	60	20	44
13	$AgNO_3$ (0.15)	CH_3CN	80	20	49
14	$AgNO_3$ (0.15)	CH_3CN	100	20	55
15	AgOTf (0.15)	CH_3CN	90	20	<5
16	Ag_2CO_3 (0.15)	CH_3CN	90	20	<5
17	$AgNO_3$ (0.15)	CH_3CN	90	40	65
18	$AgNO_3$ (0.15)	CH_3CN	90	1.0 h	70
19	**$AgNO_3$ (0.15)**	**CH_3CN**	**90**	**2.0 h**	**78**
20	$AgNO_3$ (0.15)	CH_3CN	90	3.0 h	76
21	–	CH_3CN	90	1.0 h	nr[c]

[a] Reaction conditions: (*E*)-β-nitrostyrene **1a** (0.3 mmol, 44.7 mg), diisopropyl *H*-phosphite **2a** (0.45 mmol, 74.7 mg), $AgNO_3$ as the catalyst in solvent (3.0 mL).
[b] Isolated yield.
[c] nr = no reaction.

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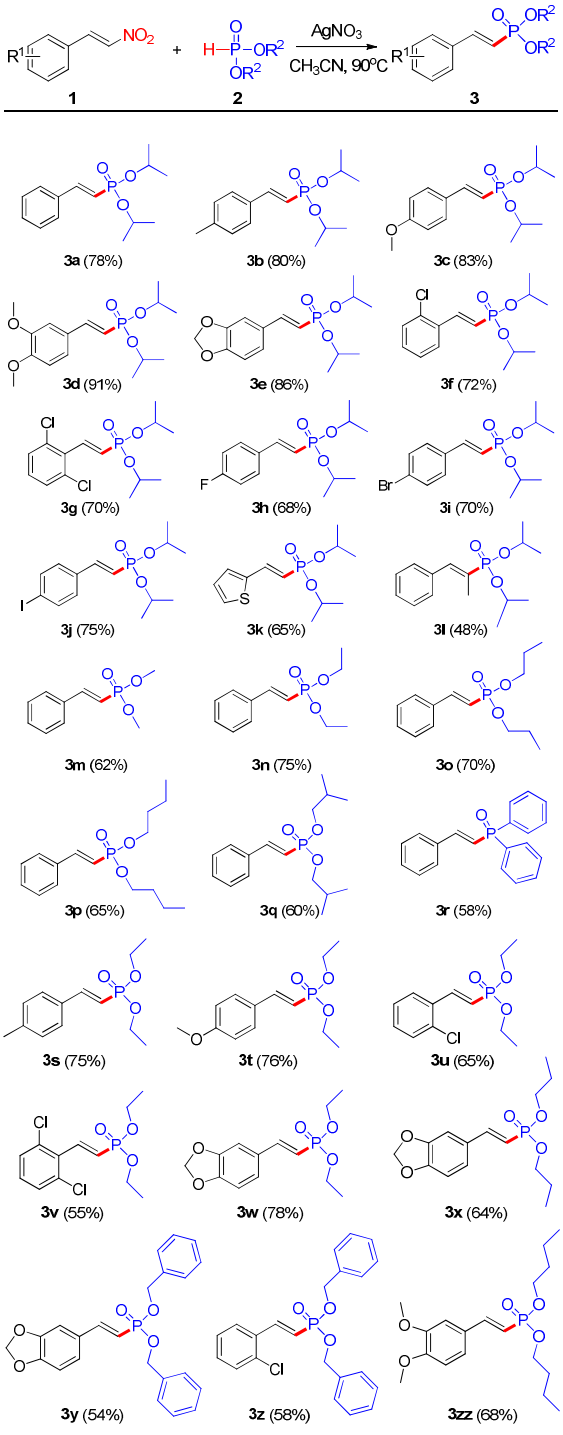
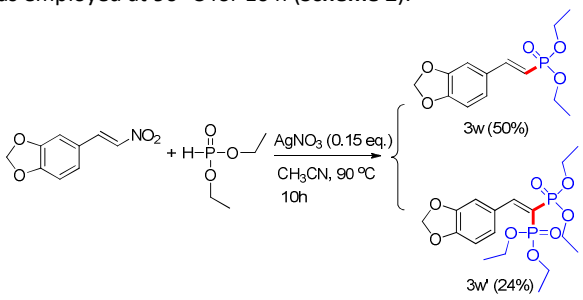
Table 2 Synthesis of 2-arylvinylphosphonates from *β*-nitrostyrenes with dialkyl *H*-phosphites[a,b]



[a] Reaction conditions: (*E*)-*β*-nitrostyrenes **1** (0.3 mmol), dialkyl *H*-phosphites **2** (0.45 mmol), $AgNO_3$ (0.045 mmol, 7.6 mg), in CH_3CN (3.0 mL) at 90 °C for 2.0 h.
[b] Isolated yields.

With the optimized conditions in hand, we next set out to examine the scope of *β*-nitrostyrenes and *H*-phosphites, and the results are summarized in **Table 2**. A range of *β*-nitrostyrene derivatives were found to undergo denitration phosphonation in good to excellent yields ranging from 48-91% with high stereoselectivity (**Table 2**, entries **3a-3l**, **3m-3zz**). Substituents such as methyl, methoxy, methylenedioxy, fluoro, chloro, bromo, and iodo groups are well tolerated on the aromatic ring and their reactions afforded the target products in good to excellent yields, showing the broad scope of this reaction. *β*-Nitrostyrenes with electron-donating groups (**Table 2**, entries **3b-3e**) could give slightly better yields than analogues with electron-withdrawing groups (**Table 2**, entries **3f-3j**). The results indicated that electron-donating groups on the phenyl ring contributed to *β*-position carbon electron density, which made it more susceptible to an electrophilic attack by the phosphonyl radical. Notably, sterically demanding substrates like (*E*)-3,4-dimethoxyl-*β*-nitrostyrenes and (*E*)-2,6-dichloro-*β*-nitrostyrenes could be phosphorylated in 91% and 70% yields (**Table 2**, entries **3d** and **3g**). However, steric hindrance will lead to lower yield when *β*-methyl-*β*-nitrostyrene is employed (**Table 2**, entry **3l**). It was gratifying to find that heterocyclic *β*-nitroalkene ((*E*)-2-(2-nitrovinyl)thiophene) also reacted smoothly with diisopropyl *H*-phosphite, leading to the corresponding product **3k** in moderated yield (65%). Unfortunately, aliphatic nitroalkenes failed to deliver the desired products with the current catalytic system.

Subsequently, the scope for various dialkyl *H*-phosphites was also investigated. The reaction could proceed smoothly using different dialkyl *H*-phosphites to form the desired products in moderate to excellent yields in 60-78% with high stereoselectivity (**Table 2**, entries **3a, 3m-3q**). It is gratifying to see that the reaction not only worked with dialkyl *H*-phosphites but also with diphenylphosphine oxide as well (**Table 2**, entry **3r**). Using the standard reaction condition, the corresponding products were produced in moderate to good yields (**Table 2**, entries **3s-3zz**). However, the yields of products **3y** and **3z** were lower when dibenzyl *H*-phosphite was employed, which was possible that partial product was hydrolyzed. Bisphosphonate drugs are used to treat a variety of bone resorption diseases, such as osteoporosis, Paget's disease, and hypercalcemia due to malignancy.[17] In the study of using (*E*)-5-(2-nitrovinyl)benzo[*d*][1,3]dioxole and diethyl *H*-phosphite as the coupling partners, we found that this resulted in a mixture of mono- **3w** (yield: 50%) and bis-phosphorylated products **3w'** (yield: 24%) when 3.0 eq. diethyl *H*-phosphite was employed at 90 °C for 10 h (**Scheme 2**).



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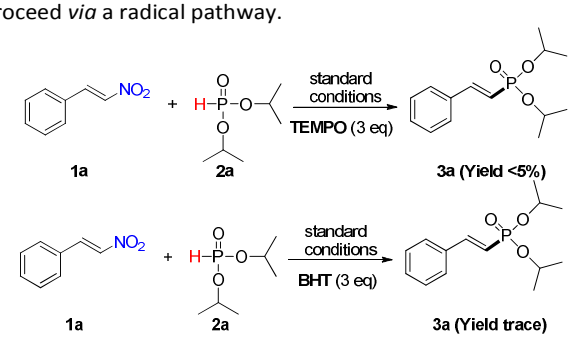
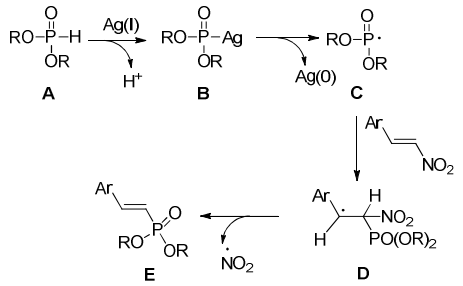
Scheme 2 Synthesis of mono- and bis-phosphorylated products

To clarify the reaction mechanism, some controlled experiments were designed to investigate this transformation (**Scheme 3**). When the reaction of (*E*)-*β*-nitrostyrene **1a** with diisopropyl *H*-phosphite **2a** was performed under the standard conditions by the addition of 3.0 eqivalents radical scavengers, such as TEMPO and BHT, and the target product **3a** decreased dramatically. These results indicated that the reaction might proceed *via* a radical pathway.



Scheme 3 Controlled experiments

Previous works have shown that silver salts can react with *H*-phosphites to form the active $(RO)_2P(O)Ag$ complexes which subsequently generate the phosphoryl radical.[16] Based on our controlled experimental results and literature precedents,[8b, 18] the following plausible mechanism can be proposed for the transformation (**Scheme 4**). The phosphoryl radical **C** may be generated from the complex **B** which itself is formed by the reaction of $AgNO_3$ catalyst with *H*-phosphites **A**. Subsequently, the radical **C** selectively adds to the *β*-position of (*E*)-*β*-nitrostyrene to form a carbon-centered radical **D**, which undergoes an elimination reaction by the leaving NO_2 radical to form the desired product **E**. Ag(0) could be oxidized back to Ag(I) by HNO_3,[16a, 18a] thus closing the catalytic cycle.



Scheme 4 Proposed reaction mechanism for the formation of 2-arylvinylphosphonates

Conclusions

In conclusion, we have developed a novel and highly stereoselectivity protocol for the synthesis of 2-arylvinylphosphonates starting from (*E*)-*β*-nitrostyrene through a tandem radical addition-denitration process. This process features a broad substrate scope and functional group tolerance. The reaction proceeded under mild conditions to afford the selective (*E*)-2-arylvinylphosphonates in moderate to good yields.

Experimental

General information

Anhydrous solvents were obtained by standard procedure. All substrates purchased from *J* & *K* Scientific Ltd. were used without further purification. Column chromatography was performed using 300-400 mesh silica with the indicated solvent system according to standard techniques. Nuclear magnetic resonance spectra were recorded on Bruker Avance 400 MHz spectrometer. Chemical shifts for ^1H NMR spectra are recorded in parts per million from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane. Chemical shift for ^{31}P NMR spectra are recorded relative to 85% H_3PO_4 (δ = 0 ppm) as external standard. High resolution mass spectra (HR MS) were obtained on Q-TOF instrument using the ESI technique. IR spectra were recorded on Shimadazu IR-408 Fourier transform infrared spectrophotometer using a thin film supported on KBr pellets. Melting points were measured on an XT4A microscopic apparatus uncorrected.

General procedure for synthesis of 2-arylvinylphosphonates (3)

(*E*)-*β*-nitrostyrenes **1** (0.3 mmol), dialkyl *H*-phosphites **2** (0.45 mmol), and $AgNO_3$ (0.045mmol, 7.6 mg) in CH_3CN (3.0 mL) were added to a 25 mL Schlenk tube. The mixture was heated at 90 °C for 2.0 h (monitored by TLC). After completion of the reaction, the solvent was distilled under vacuum. 10 mL ethylacetate was added to the residuum, 15 mL 5% $NaHCO_3$ was added to wash two times, and 10 mL saturated NaCl solution washed one time. The organic phase was dried over anhydrous $NaSO_4$ and concentrated under vacuum. The crude product was purified by silica gel column chromatography to give the desired products **3** using ethyl acetate/petroleum ether (1:3 to 2:1) as eluant.

(E)-Diisopropyl styrylphosphonate (3a)[8b]

Colorless viscous liquid. IR (KBr) ν(cm^{-1}): 2978, 2933 (-CH_3), 1614, 1450 (Ar-), 1246 (P=O), 1105 (P-O). ^1H NMR ($CDCl_3$) δ: 7.53-7.43 (m, 3H), 7.39-7.31 (m, 3H), 6.27 (t, *J* = 17.6 Hz, 1H), 4.75-4.67 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 147.8 (d, J_{P-C} = 6.6 Hz), 134.9 (d, J_{P-C} = 22.9 Hz), 130.0, 128.7, 127.6, 115.5 (d, J_{P-C} = 190.9 Hz), 70.4 (d, J_{P-C} = 5.5 Hz), 24.0 (d, J_{P-C} = 4.1 Hz), 23.9 (d, J_{P-C} = 4.8 Hz). ^{31}P NMR ($CDCl_3$) δ: 17.4. MS (ESI) m/z: 269.3 $[M + H]^+$ (calcd for $C_{14}H_{22}O_3P^+$ 269.1).

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***(E)-Diisopropyl 4-methylstyrylphosphonate* (3b)[7b]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3126, 2978 (-CH_3), 1616, 1400 (Ar-), 1246 (P=O), 1107 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.46 (dd, *J* = 22.6 Hz, *J* = 17.4 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.20 (t, *J* = 17.5 Hz, 1H), 4.75-4.66 (m, 2H), 2.36 (s, 3H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 147.8 (d, J_{P-C} = 6.7 Hz), 140.4, 132.3 (d, J_{P-C} = 23.3 Hz), 129.5, 127.6, 114.2 (d, J_{P-C} = 191.5 Hz), 70.4 (d, J_{P-C} = 5.6 Hz), 24.1 (d, J_{P-C} = 4.1 Hz), 24.0 (d, J_{P-C} = 4.7 Hz), 21.4. ^{31}P NMR ($CDCl_3$) δ: 17.8. MS (ESI) m/z: 283.2 [M + H]$^+$ (calcd for $C_{15}H_{24}O_3P^+$ 283.1).

***(E)-Diisopropyl 4-methoxystyrylphosphonate* (3c)[7b]**

Colorless viscous liquid. IR (KBr) ν(cm^{-1}): 2980, 2923 (-CH_3), 1610, 1455 (Ar-), 1244 (P=O), 1103 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.49-7.32 (m, 3H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.10 (t, *J* = 17.4 Hz, 1H), 4.74-4.66 (m, 2H), 3.82 (s, 3H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 161.1, 147.5 (d, J_{P-C} = 6.8 Hz), 129.2, 127.7 (d, J_{P-C} = 23.5 Hz), 114.1, 112.2 (d, J_{P-C} = 192.4 Hz), 70.3 (d, J_{P-C} = 5.4 Hz), 55.3, 24.0 (d, J_{P-C} = 4.0 Hz), 23.9 (d, J_{P-C} = 4.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 18.3. MS (ESI) m/z: 299.2 [M + H]$^+$ (calcd for $C_{15}H_{24}O_4P^+$ 299.1).

***(E)-Diisopropyl 3,4-dimethoxystyrylphosphonate* (3d)[19]**

Light yellow solid, m.p. 75-76 °C (from chloroform). IR (KBr) ν(cm^{-1}): 2989, 2954 (-CH_3), 1613, 1458 (Ar-), 1233(P=O), 1074 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.36 (dd, *J* = 22.5 Hz, *J* = 17.4 Hz, 1H), 7.03 (dd, *J* = 8.2 Hz, *J* = 1.8 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.06 (t, *J* = 17.4 Hz, 1H), 4.70-4.62 (m, 2H), 3.86 (s, 6H), 1.32 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 150.8, 149.1, 147.6 (d, J_{P-C} = 6.9 Hz, CH), 128.0 (d, J_{P-C} = 23.5 Hz), 121.9 (CH), 112.8 (d, J_{P-C} = 192.5 Hz, CH), 110.9 (CH), 109.3 (CH), 70.3 (d, J_{P-C} = 5.4 Hz), 55.9 (CH_3), 55.8 (CH_3), 24.1 (d, J_{P-C} = 4.2 Hz, CH_3), 24.0 (d, J_{P-C} = 4.2 Hz, CH_3). ^{31}P NMR ($CDCl_3$) δ: 18.0. MS (ESI) m/z: 329.2 [M + H]$^+$ (calcd for $C_{16}H_{26}O_5P^+$ 329.1).

***(E)-Diisopropyl (2-(benzo[d][1,3]dioxol-5-yl)vinyl)phosphonate* (3e)[6c]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3120, 2978, 2933 (-CH_3, -CH_2), 1601, 1491, 1448 (Ar-), 1254 (P=O), 1105 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.37 (dd, *J* = 22.4 Hz, *J* = 17.4 Hz, 1H), 7.00 (d, *J* = 1.1 Hz, 1H), 6.96 (d, *J* = 9.3 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.07 (t, *J* = 17.2 Hz, 1H), 5.99 (s, 2H), 4.74-4.65 (m, 2H), 1.36 (d, *J* = 6.2 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 149.3, 148.2, 147.3 (d, J_{P-C} = 7.2 Hz, CH), 129.4 (d, J_{P-C} = 23.8 Hz), 123.7 (CH), 113.0 (d, J_{P-C} = 192.1 Hz, CH), 107.2 (d, J_{P-C} = 225.5 Hz, CH), 101.4 (CH), 70.3 (d, J_{P-C} = 5.5 Hz), 24.0 (d, J_{P-C} = 4.0 Hz, CH_3), 23.9 (d, J_{P-C} = 4.2 Hz, CH_3). ^{31}P NMR ($CDCl_3$) δ: 17.8. MS (ESI) m/z: 313.3 [M + H]$^+$ (calcd for $C_{15}H_{22}O_5P^+$ 313.1).

***(E)-Diisopropyl 2-chlorostyrylphosphonate* (3f)**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3128, 2979 (-CH_3), 1614, 1450, 1367 (Ar-), 1248 (P=O), 1105 (P-O), 754 (C-Cl). ^{1}H NMR ($CDCl_3$) δ: 7.83 (dd, *J* = 22.6 Hz, *J* = 17.5 Hz, 1H), 7.60-7.57 (m, 1H), 7.40-7.38 (m, 1H), 7.31-7.27 (m, 2H), 6.31 (t, *J* = 17.6 Hz, 1H), 4.79-4.70 (m, 2H), 1.36 (dd, *J* = 12.7 Hz, *J* = 6.2 Hz, 12H). ^{13}C NMR ($CDCl_3$) δ: 143.0 (d, J_{P-C} = 7.8 Hz), 134.4, 133.2 (d, J_{P-C} = 23.7 Hz), 130.8, 130.0 (d, J_{P-C} = 1.0 Hz), 127.3, 127.0, 119.8, 117.9, 70.7 (d, J_{P-C} = 5.7 Hz), 24.1 (d, J_{P-C} = 4.0 Hz), 24.0 (d, J_{P-C} = 4.8 Hz). ^{31}P NMR ($CDCl_3$) δ: 16.0. HR MS (ESI) m/z: 303.0914 [M + H]$^+$ (calcd for $C_{14}H_{21}ClO_3P^+$ 303.0911).

***(E)-Diisopropyl 2,6-dichlorostyrylphosphonate* (3g)**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3120, 3020 (-CH_3), 1610, 1589 (Ar-), 1252 (P=O), 1153 (P-O) , 756 (C-Cl). ^{1}H NMR ($CDCl_3$) δ: 7.51 (dd, *J* = 23.6 Hz, *J* = 17.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.43 (t, *J* = 18.0 Hz, 1H), 4.80-4.72 (m, 2H), 1.38 (d, *J* = 6.2 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 141.3 (d, J_{P-C} = 7.8 Hz), 134.5 (d, J_{P-C} = 1.5 Hz), 132.8 (d, J_{P-C} = 23.4 Hz), 129.6, 128.7, 125.8 (d, J_{P-C} = 183.2 Hz), 70.5 (d, J_{P-C} = 5.4 Hz), 24.1 (d, J_{P-C} = 4.0 Hz), 23.9 (d, J_{P-C} = 4.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 14.6. HR MS (ESI) m/z: 337.0518 [M + H]$^+$ (calcd for $C_{14}H_{20}Cl_2O_3P^+$ 337.0522).

***(E)-diisopropyl 4-fluorostyrylphosphonate* (3h)[7b]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3082, 2930 (-CH_3), 1614, 1457 (Ar-), 1248 (P=O), 1108 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.45-7.34 (m, 3H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.14 (t, *J* = 17.2 Hz, 1H), 4.71-4.63 (m, 2H), 1.32 (d, *J* = 6.2 Hz, 6H), 1.28 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 163.7 (d, J_{F-C} = 249.1 Hz), 146.4 (d, J_{P-C} = 6.9 Hz, CH), 131.2 (dd, J_{F-C} = 3.4 Hz, J_{P-C} = 23.5 Hz), 129.4 (d, J_{P-C} = 8.4 Hz, CH), 115.8 (d, J_{P-C} = 21.8 Hz, CH), 115.3 (dd, J_{F-C} = 2.0 Hz, J_{P-C} = 191.7 Hz, CH), 70.5 (d, J_{P-C} = 5.5 Hz, CH), 24.0 (d, J_{P-C} = 4.0 Hz, CH_3), 23.9 (d, J_{P-C} = 4.0 Hz, CH_3). ^{31}P NMR ($CDCl_3$) δ: 17.0. ^{19}F NMR ($CDCl_3$) δ: -110.2. MS (ESI) m/z: 287.3 [M + H]$^+$ (calcd for $C_{14}H_{21}FO_3P^+$ 287.1).

***(E)-diisopropyl 4-bromostyrylphosphonate* (3i)[8b]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3325, 2960 (-CH_3), 1616 (Ar-), 1250 (P=O), 1116 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.51-7.39 (m, 3H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.24 (t, *J* = 17.2 Hz, 1H), 4.76-4.66 (m, 2H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.30 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 146.4 (d, J_{P-C} = 7.0 Hz), 133.9 (d, J_{P-C} = 23.5 Hz), 132.0, 129.0, 124.2, 116.2 (d, J_{P-C} = 191.5 Hz), 70.5 (d, J_{P-C} = 5.8 Hz), 24.0 (d, J_{P-C} = 4.0 Hz), 23.9 (d, J_{P-C} = 4.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 16.6. MS (ESI) m/z: 347.2 [M + H]$^+$ (calcd for $C_{14}H_{21}BrO_3P^+$ 347.0).

***(E)-diisopropyl 4-iodostyrylphosphonate* (3j)**

Yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3028, 2965 (-CH_3), 1624, 1547 (Ar-), 1246 (P=O), 1109 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.70 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 17.6 Hz, *J* = 22.6 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.25 (t, *J* = 17.2 Hz, 1H), 4.73-4.65 (m, 2H), 1.35 (d, *J* = 6.2 Hz, 6H), 1.30 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 146.4 (d, J_{P-C} = 6.7 Hz), 138.0, 134.5 (d, J_{P-C} = 23.3 Hz), 129.1, 127.6, 116.6 (d, J_{P-C} = 191.0 Hz), 70.6 (d, J_{P-C} = 5.7 Hz), 24.1 (d, J_{P-C} = 4.0 Hz), 24.0 (d, J_{P-C} = 4.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 16.6. HR MS (ESI) m/z: 395.0270 [M + H]$^+$ (calcd for $C_{14}H_{21}IO_3P^+$395.0268).

***(E)-diisopropyl (2-(thiophen-2-yl)vinyl)phosphonate* (3k)[7b]**

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Colorless viscous liquid. IR (KBr) ν(cm^{-1}): 3007, 2926 (-CH_3), 1613, 1452 (Ar-), 1245 (P=O), 1103 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.49 (dd, *J* = 22.6 Hz, *J* = 17.4 Hz, 1H), 7.28 (d, *J* = 5.0 Hz, 1H), 7.13 (d, *J* = 3.3 Hz, 1H), 6.97 (t, *J* = 4.6 Hz, 1H), 5.95 (t, *J* = 16.8 Hz, 1H), 4.69-4.59 (m, 2H), 1.30 (d, *J* = 6.2 Hz, 6H), 1.26 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 140.5 (d, J_{P-C} = 26.7 Hz), 140.2 (d, J_{P-C} = 7.6 Hz, CH), 129.9 (CH), 127.9 (d, J_{P-C} = 1.1 Hz, CH), 127.8, 114.1 (d, J_{P-C} = 193.1 Hz, CH), 70.5 (d, J_{P-C} = 5.5 Hz, CH), 24.0 (d, J_{P-C} = 4.0 Hz, CH_3), 23.9 (d, J_{P-C} = 4.0 Hz, CH_3). ^{31}P NMR ($CDCl_3$) δ: 16.7. MS (ESI) m/z: 275.2 $[M + H]^+$ (calcd for $C_{12}H_{20}O_3PS^+$ 275.0).

***(E)-diisopropyl (1-phenylprop-1-en-2-yl)phosphonate* (3l)**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3125, 3018 (-CH_3), 1612, 1576 (Ar-), 1250 (P=O), 1132 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.47 (dd, *J* = 24.8 Hz, *J* = 1.4 Hz, 1H), 7.38 (d, *J* = 4.4 Hz, 4H), 7.34-7.29 (m, 1H), 4.71-4.68 (m, 2H), 2.06 (dd, *J* = 15.2 Hz, *J* = 1.4 Hz, 1H), 1.38 (d, *J* = 6.2 Hz, 6H), 1.31 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 141.9 (d, J_{P-C} = 12.5 Hz, CH), 135.9 (d, J_{P-C} = 23.4 Hz), 129.4 (CH), 128.4 (CH), 128.2 (CH), 126.4, 70.3 (d, J_{P-C} = 6.4 Hz, CH), 24.1 (d, J_{P-C} = 4.2 Hz, CH_3), 23.8 (d, J_{P-C} = 4.5 Hz, CH_3), 14.4 (d, J_{P-C} = 9.7 Hz, CH_3). ^{31}P NMR ($CDCl_3$) δ: 19.7. HR MS (ESI) m/z: 283.1456 $[M + H]^+$ (calcd for $C_{15}H_{24}O_3P^+$ 283.1458).

***(E)-Dimethyl styrylphosphonate* (3m)[20]**

Colorless viscous liquid. IR (KBr) ν(cm^{-1}): 2952, 2850 (-CH_3), 1616, 1448 (Ar-), 1250 (P=O), 1053 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.58-7.48 (m, 3H), 7.40-7.37 (m, 3H), 6.23 (t, *J* = 17.7 Hz, 1H), 3.78 (d, *J* = 11.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 149.6 (d, J_{P-C} = 6.6 Hz), 134.6 (d, J_{P-C} = 23.1 Hz), 130.4, 128.9, 127.7, 112.3 (d, J_{P-C} = 191.2 Hz), 52.4 (d, J_{P-C} = 5.6 Hz). ^{31}P NMR ($CDCl_3$) δ: 22.4. MS (ESI) m/z: 213.1 $[M + H]^+$ (calcd for $C_{10}H_{14}O_3P^+$ 213.0).

***(E)-Diethyl styrylphosphonate* (3n)[8b]**

Colorless viscous liquid. IR (KBr) ν(cm^{-1}): 3107, 1985 (-CH_3, -CH_2), 1610, 1545, 1464 (Ar-), 1214 (P=O), 1134 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.56-7.46 (m, 3H), 7.40-7.37 (m, 3H), 6.26 (t, *J* = 17.6 Hz, 1H), 4.17-4.09 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 148.7 (d, J_{P-C} = 6.7 Hz), 134.8 (d, J_{P-C} = 23.0 Hz), 130.2, 128.8, 127.7, 113.9 (d, J_{P-C} = 190.3 Hz), 61.8 (d, J_{P-C} = 5.5 Hz), 16.4 (d, J_{P-C} = 6.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 19.5. MS (ESI) m/z: 241.3 $[M + H]^+$ (calcd for $C_{12}H_{18}O_3P^+$ 241.1).

***(E)-Dipropyl styrylphosphonate* (3o)[7a]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3122, 2970 (-CH_3, -CH_2), 1616, 1400 (Ar-), 1244 (P=O), 1065 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.56-7.46 (m, 3H), 7.39-7.37 (m, 3H), 6.26 (t, *J* = 17.6 Hz, 1H), 4.05-3.99 (m, 4H), 1.76-1.68 (m, 4H), 0.97 (d, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 148.8 (d, J_{P-C} = 6.7 Hz), 134.8 (d, J_{P-C} = 23.2 Hz), 130.3, 128.9, 127.7, 113.6 (d, J_{P-C} = 191.0 Hz), 67.4 (d, J_{P-C} = 5.8 Hz), 23.8 (d, J_{P-C} = 6.5 Hz), 10.0. ^{31}P NMR ($CDCl_3$) δ: 19.6. MS (ESI) m/z: 269.2 $[M + H]^+$ (calcd for $C_{14}H_{22}O_3P^+$ 269.1).

***(E)-dibutyl styrylphosphonate* (3p)[7b]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3128, 2962 (-CH_3, -CH_2), 1526, 1415 (Ar-), 1248 (P=O), 1068 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.52-7.42 (m, 3H), 7.36-7.33 (m, 3H), 6.24 (t, *J* = 17.6 Hz, 1H), 4.06-3.98 (m, 4H), 1.67-1.60 (m, 4H), 1.43-1.35 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 148.7 (d, J_{P-C} = 6.6 Hz, CH), 134.8 (d, J_{P-C} = 23.1 Hz), 130.2 (CH), 128.8 (CH), 127.7 (CH), 113.8 (d, J_{P-C} = 190.4 Hz, CH), 65.5 (d, J_{P-C} = 5.7 Hz, CH_2), 32.5 (d, J_{P-C} = 6.3 Hz, CH_2), 18.7 (CH_2), 13.6 (CH_3). ^{31}P NMR ($CDCl_3$) δ: 19.6. MS (ESI) m/z: 297.3 $[M + H]^+$ (calcd for $C_{16}H_{26}O_3P^+$ 297.1).

***(E)-Diisobutyl styrylphosphonate* (3q)**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3124, 2969 (-CH_3, -CH_2), 1608, 1410 (Ar-), 1167 (P=O), 1047 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.57-7.47 (m, 3H), 7.39-7.37 (m, 3H), 6.26 (t, *J* = 17.6 Hz, 1H), 3.85-3.80 (m, 4H), 2.00-1.93 (m, 2H), 0.95 (d, *J* = 6.8 Hz, 9H). ^{13}C NMR ($CDCl_3$) δ: 148.9 (d, J_{P-C} = 6.5 Hz), 134.8 (d, J_{P-C} = 23.3 Hz), 130.3, 128.9, 127.7, 113.4 (d, J_{P-C} = 191.7 Hz), 71.9 (d, J_{P-C} = 6.1 Hz), 29.1 (d, J_{P-C} = 6.7 Hz), 18.7 (d, J_{P-C} = 1.9 Hz). ^{31}P NMR ($CDCl_3$) δ: 19.4. HR MS (ESI) m/z: 297.1618 $[M + H]^+$ (calcd for $C_{16}H_{26}O_3P^+$ 297.1614).

***(E)-diphenyl(styryl)phosphine oxide* (3r)[8b]**

Light yellow solid, m.p. 145-146 °C (from chloroform). IR (KBr) ν(cm^{-1}): 1606, 1437, 1400 (Ar-), 1162 (P=O), 1120 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.77-7.72 (m, 4H), 7.55-7.44 (m, 9H), 7.36-7.35 (m, 3H), 6.83 (dd, *J* = 22.4 Hz, *J* = 17.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 147.6 (d, J_{P-C} = 3.5 Hz, CH), 135.1 (d, J_{P-C} = 17.8 Hz), 132.8 (d, J_{P-C} = 105.5 Hz), 131.9 (d, J_{P-C} = 2.5 Hz, CH), 131.4 (d, J_{P-C} = 10.0 Hz, CH), 130.1, 128.8 (d, J_{P-C} = 27.8 Hz, CH), 128.7 (CH), 127.8 (CH), 119.0 (d, J_{P-C} = 103.9 Hz, CH). ^{31}P NMR ($CDCl_3$) δ: 24.8. MS (ESI) m/z: 305.0 $[M + H]^+$ (calcd for $C_{20}H_{18}OP^+$ 305.1).

***(E)-Diethyl 4-methylstyrylphosphonate* (3s)[8b]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3128, 2969 (-CH_3, -CH_2), 1616, 1405 (Ar-), 1246 (P=O), 1026 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.47 (dd, *J* = 22.6 Hz, *J* = 17.5 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.19 (t, *J* = 17.7 Hz, 1H), 4.16-4.08 (m, 4H), 2.37 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 148.8 (d, J_{P-C} = 6.6 Hz), 140.6, 132.1 (d, J_{P-C} = 23.2 Hz), 129.5, 127.7, 112.4 (d, J_{P-C} = 190.8 Hz), 61.8 (d, J_{P-C} = 5.4 Hz), 21.4, 16.4 (d, J_{P-C} = 6.5 Hz). ^{31}P NMR ($CDCl_3$) δ: 19.9. MS (ESI) m/z: 255.0 $[M + H]^+$ (calcd for $C_{13}H_{20}O_3P^+$ 255.1).

***(E)-Diethyl 4-methoxystyrylphosphonate* (3t)[8b]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3134, 2969 (-CH_3, -CH_2), 1604, 1512, 1400 (Ar-), 1257 (P=O), 1028 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.46-7.36 (m, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.05 (t, *J* = 17.6 Hz, 1H), 4.12-4.04 (m, 4H), 3.79 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 161.2, 148.4 (d, J_{P-C} = 6.9 Hz, CH), 129.3 (CH), 127.6 (d, J_{P-C} = 23.7 Hz), 114.2 (CH), 110.6 (d, J_{P-C} = 191.7 Hz, CH), 61.7 (d, J_{P-C} = 5.3 Hz, CH_2), 55.3 (CH_3), 16.4 (d, J_{P-C} = 6.5 Hz, CH_3). ^{31}P NMR ($CDCl_3$) δ: 20.4. MS (ESI) m/z: 271.3 $[M + H]^+$ (calcd for $C_{13}H_{20}O_4P^+$ 271.1).

***(E)-Diethyl 2-chlorostyrylphosphonate* (3u)[8a]**

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Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3132, 2969 (-CH_3, -CH_2), 1595, 1401 (Ar-), 1254 (P=O), 1075 (P-O), 806 (C-Cl). ^{1}H NMR ($CDCl_3$) δ: 7.86 (dd, *J* = 22.6 Hz, *J* = 17.5 Hz, 1H), 7.61-7.58 (m, 1H), 7.41-7.39 (m, 1H), 7.31-7.28 (m, 2H), 6.30 (t, *J* = 17.7 Hz, 1H), 4.20-4.12 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 144.0 (d, J_{P-C} = 7.8 Hz), 134.5, 133.2 (d, J_{P-C} = 23.5 Hz), 131.0, 130.0, 127.4, 127.0, 117.2 (d, J_{P-C} = 33.0 Hz), 62.1 (d, J_{P-C} = 5.6 Hz), 16.4 (d, J_{P-C} = 6.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 18.2. MS (ESI) m/z: 275.2 [M + H]$^+$ (calcd for $C_{12}H_{17}ClO_3P^+$ 275.0).

***(E)-Diethyl 2,6-dichlorostyrylphosphonate* (3v)[8a]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3125, 3018 (-CH_3, -CH_2), 1615, 1578 (Ar-), 1250 (P=O), 1151 (P-O) , 764 (C-Cl). ^{1}H NMR ($CDCl_3$) δ: 7.53 (dd, *J* = 23.7 Hz, *J* = 17.9 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 8.2 Hz, 1H), 6.42 (t, *J* = 18.2 Hz, 1H), 4.21-4.14 (m, 4H), 1.38 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 142.1 (d, J_{P-C} = 7.6 Hz), 134.5 (d, J_{P-C} = 1.4 Hz), 129.8, 128.7, 127.9, 124.2 (d, J_{P-C} = 182.5 Hz), 62.2 (d, J_{P-C} = 5.4 Hz), 16.4 (d, J_{P-C} = 6.4 Hz). ^{31}P NMR ($CDCl_3$) δ: 17.0. MS (ESI) m/z: 309.2 [M + H]$^+$ (calcd for $C_{12}H_{16}Cl_2O_3P^+$ 309.0).

***(E)-diethyl (2-(benzo[d][1,3]dioxol-5-yl)vinyl)phosphonate* (3w)[21]**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3138, 2969 (-CH_3, -CH_2), 1603, 1590, 1401 (Ar-), 1254 (P=O), 1038 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.33 (dd, *J* = 22.4 Hz, *J* = 17.4 Hz, 1H), 6.94 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.98 (t, *J* = 17.4 Hz, 1H), 5.93 (s, 2H), 4.09-4.01 (m, 4H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 149.4, 148.4, 148.3 (d, J_{P-C} = 3.8 Hz, CH), 129.3 (d, J_{P-C} = 23.8 Hz), 123.9 (CH), 112.3 (CH), 110.4 (CH), 108.4 (CH), 106.2 (CH), 101.5 (CH_2), 61.7 (d, J_{P-C} = 5.5 Hz, CH_2), 16.3 (d, J_{P-C} = 6.4 Hz, CH_3). ^{31}P NMR ($CDCl_3$) δ: 19.6. MS (ESI) m/z: 285.2 [M + H]$^+$ (calcd for $C_{13}H_{18}O_5P^+$ 285.0).

***Tetraethyl (2-(benzo[d][1,3]dioxol-5-yl)ethene-1,1-diyl)bis(phosphonate)* (3w')**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3122, 2987 (-CH_3, -CH_2), 1603, 1405 (Ar-), 1254 (P=O), 1106 (P-O). ^{1}H NMR ($CDCl_3$) δ: 8.18 (dd, *J* = 29.4 Hz, *J* = 47.7 Hz, 1H), 7.55 (d, *J* = 1.3 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.83 (s, 2H), 4.22-4.14 (m, 4H), 4.13-4.05 (m, 4H), 1.37 (t, *J* = 7.0 Hz, 6H), 1.24 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 161.1 (d, J_{P-C} = 2.2 Hz), 150.1, 147.6, 128.3 (dd, J_{P-C} = 22.6 Hz, J_{P-C} = 8.8 Hz), 127.8, 110.6, 107.9, 101.6, 62.6 (d, J_{P-C} = 5.2 Hz), 62.4 (d, J_{P-C} = 5.8 Hz), 16.3 (d, J_{P-C} = 6.6 Hz), 16.1 (d, J_{P-C} = 6.6 Hz). ^{31}P NMR ($CDCl_3$) δ: 18.3 (d, J_{P-P} = 49.5 Hz), 12.8 (d, J_{P-P} = 49.5 Hz). HR MS (ESI) m/z: 421.1178 [M + H]$^+$ (calcd for $C_{17}H_{27}O_8P_2^+$ 421.1176).

***(E)-Dipropyl (2-(benzo[d][1,3]dioxol-5-yl)vinyl)phosphonate* (3x)**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3140, 2967 (-CH_3, -CH_2), 1607, 1582, 1406 (Ar-), 1247 (P=O), 1036 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.40 (dd, *J* = 22.4 Hz, *J* = 17.4 Hz, 1H), 7.01 (d, *J* = 1.3 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.09-6.00 (m, 3H), 4.03-3.97 (m, 4H), 1.76-1.67 (m, 4H), 0.96 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 149.4, 148.3 (d, J_{P-C} = 5.0 Hz), 129.3 (d, J_{P-C} = 23.7 Hz), 123.9, 112.3, 110.4, 108.4, 106.2, 101.5, 67.3 (d, J_{P-C} = 5.5 Hz), 23.8 (d, J_{P-C} = 6.5 Hz), 10.1. ^{31}P NMR ($CDCl_3$) δ: 20.1. HR MS (ESI) m/z: 313.1202 [M + H]$^+$ (calcd for $C_{15}H_{22}O_5P^+$ 313.1199).

***(E)-Dibenzyl (2-(benzo[d][1,3]dioxol-5-yl)vinyl)phosphonate* (3y)**

Light yellow solid, m.p. 106-107 °C (from chloroform). IR (KBr) ν(cm^{-1}): 3126, 3033 (-CH_2), 1601, 1491, 1448, 1400 (Ar-), 1254 (P=O), 1036 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.38-7.29 (m, 11H), 6.90-6.87 (m, 2H), 6.76 (d, *J* = 7.9 Hz, 1H), 6.01 (t, *J* = 17.6 Hz, 1H), 5.96 (s, 2H), 5.07 (s, 2H), 5.05 (s, 2H). ^{13}C NMR ($CDCl_3$) δ: 149.6, 148.7 (d, J_{P-C} = 7.2 Hz, CH), 136.3 (d, J_{P-C} = 6.6 Hz), 129.2 (d, J_{P-C} = 24.4 Hz), 128.6 (CH), 128.4 (CH), 127.9 (CH), 124.0 (CH), 111.0 (d, J_{P-C} = 192.8 Hz, CH), 108.4 (CH), 106.2 (CH), 101.5 (CH_2), 67.4 (d, J_{P-C} = 5.2 Hz, CH_2). ^{31}P NMR ($CDCl_3$) δ: 21.1. HR MS (ESI) m/z: 409.1196 [M + H]$^+$ (calcd for $C_{23}H_{22}O_5P^+$ 409.1199).

***(E)-Dibenzyl 2-chlorostyrylphosphonate* (3z)**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3126 (-CH_2), 1603, 1401 (Ar-), 1250 (P=O), 1049 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.87 (dd, *J* = 23.0 Hz, *J* = 17.5 Hz, 1H), 7.47 (dd, *J* = 7.5 Hz, *J* = 1.6 Hz, 1H), 7.39-7.24 (m, 13H), 6.24 (t, *J* = 18.1 Hz, 1H), 5.11 (d, *J* = 2.8 Hz, 2H), 5.09 (d, *J* = 2.7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ: 144.4 (d, J_{P-C} = 8.1 Hz, CH), 136.1 (d, J_{P-C} = 6.5 Hz), 134.6, 133.0 (d, J_{P-C} = 23.9 Hz), 131.0 (CH), 130.1 (CH), 128.6 (CH), 128.4 (CH), 128.0 (CH), 127.4 (d, J_{P-C} = 1.0 Hz, CH), 127.0 (CH), 116.9 (d, J_{P-C} = 190.9 Hz, CH), 67.5 (d, J_{P-C} = 5.6 Hz, CH_2). ^{31}P NMR ($CDCl_3$) δ: 19.2. HR MS (ESI) m/z: 399.0909 [M + H]$^+$ (calcd for $C_{22}H_{21}ClO_3P^+$ 399.0911).

***(E)-dibutyl 3,4-dimethoxystyrylphosphonate* (3zz)**

Light yellow viscous liquid. IR (KBr) ν(cm^{-1}): 3147, 2962 (-CH_3, -CH_2), 1514, 1400 (Ar-), 1269 (P=O), 1159 (P-O). ^{1}H NMR ($CDCl_3$) δ: 7.37 (dd, *J* = 22.4 Hz, *J* = 17.4 Hz, 1H), 7.02 (dd, *J* = 8.2 Hz, *J* = 1.5 Hz, 1H), 6.98 (d, *J* = 1.5 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.04 (t, *J* = 17.4 Hz, 1H), 4.03-3.96 (m, 4H), 3.85 (s, 6H), 1.66-1.59 (m, 4H), 1.41-1.32 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 150.9, 149.1, 148.5 (d, J_{P-C} = 6.9 Hz, CH), 127.8 (d, J_{P-C} = 23.5 Hz), 122.0 (CH), 111.0 (d, J_{P-C} = 191.9 Hz, CH), 110.9 (CH), 109.3 (CH), 65.5 (CH_3), 65.4 (CH_3), 55.9 (d, J_{P-C} = 8.9 Hz, CH_2), 32.5 (d, J_{P-C} = 6.5 Hz, CH_2), 18.7 (CH_2), 13.6 (CH_3). ^{31}P NMR ($CDCl_3$) δ: 19.8. HR MS (ESI) m/z: 357.1823 [M + H]$^+$ (calcd for $C_{18}H_{30}O_5P^+$ 357.1825).

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Graphic Abstract

Silver-catalyzed synthesis of 2-arylvinylphosphonates by cross-coupling of β-nitrostyrenes with *H*-phosphites

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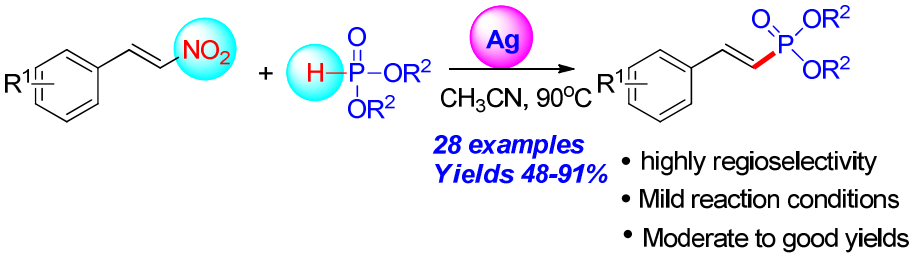

An efficient protocol for stereoselective synthesis of vinylphosphonates has been developed via $AgNO_3$-catalyzed cross-coupling of β-nitrostyrenes with dialkyl *H*-phosphites under mild conditions.