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Synthesis of Alkenylphosphonates through Palladium-Catalyzed Coupling of α-Diazo Phosphonates with Benzyl or Allyl Halides

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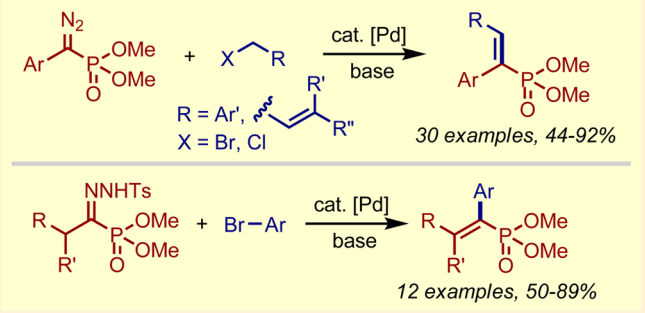
Supporting Information

ABSTRACT: An efficient method for the synthesis of organophosphonates through palladium-catalyzed coupling of α-diazo phosphonates with benzyl or allyl halides has been developed. Trisubstituted alkenylphosphonates bearing versatile functional groups can be easily accessed in good yields and with excellent stereoselectivity through this method. Moreover, with similar strategy α-substituted vinylphosphonates can also be attained by the palladium-catalyzed coupling reaction of *N*-tosylhydrazones and aryl bromides. Migratory insertion of palladium carbene is proposed as the key step in this reaction.



INTRODUCTION

Organophosphonates have attracted much attention for their important roles in biochemistry, pharmaceuticals and agrochemicals.[1] Among them, alkenylphosphonates are essential structural units as well as synthetic precursors, which can undergo various transformations to afford biologically active compounds and other functional molecules.[2] Because of their important applications in chemistry and biology, significant efforts have been devoted to the development of synthetic methods toward this type of compounds. Conventionally, alkenylphosphonates with defined stereochemistry can be prepared by Wittig, Wittig−Horner or metal-catalyzed Michaelis−Arbusov reactions.[3] Other strategies include Heck-type reaction of alkenylphosphonates with various coupling partners,[4] cross-coupling of P(O)H compounds with vinyl halides,[5] olefin metathesis[6] and so on.[7] However, these methods in general suffer from the drawbacks such as relatively harsh reaction conditions and low yields of the products, along with the need to prepare prefunctionalized alkenylphosphonates. Recently, transition-metal-catalyzed addition of hydrogen phosphonates to alkynes has become an efficient way to synthesize alkenylphosphonates,[8] but in most cases only terminal alkynes are effective and the regioselectivity remains a serious problem in the reaction of internal alkynes. In addition, methods to synthesize trisubstituted alkenylphosphonates are still limited. Thus, the development of efficient and complementary strategy with mild reaction conditions and easily accessible reagents remains a topic of great interest.

Diazo compounds, which have been commonly utilized as carbene precursors, have recently emerged as a novel type of coupling partners in organic synthesis.[9] In particular, palladium-catalyzed cross-coupling reaction via diazo compound has been established as a powerful method for the carbon−carbon double bond formations.[10−12] As a continuation of our own interests in the carbene involved cross-coupling reactions, we envisioned that alkenylphosphonates should be accessed by applying the strategy with easily available α-diazo arylmethylphosphonates[13] as the coupling partners. As shown in Scheme 1, the coupling reaction is considered to follow similar pathway involving oxidative addition, palladium carbene formation, migratory insertion and β-hydride elimination. Herein we report the development of an efficient synthesis of alkenylphosphonates with good yields and excellent stereoselectivity through Pd-catalyzed coupling of α-diazo arylmethylphosphonates with benzyl and ally halides. The method can also be extended to the coupling reaction of *N*-tosylhydrazones with aryl bromides.

RESULTS AND DISCUSSION

Our investigation began with the reaction between α-diazo benzylphosphonates **1a** and benzyl bromide **2a** (Table 1). Various palladium catalysts with the combination of $P(2\text{-furyl})_3$ in toluene were examined, and $Pd(OAc)_2$ turned out to be more effective in this transformation (entries 1−3). Switch of the solvent from toluene to dioxane did not improve the yield (entry 4). It was observed that the main difficulty was the oxidation of the $P(2\text{-furyl})_3$ ligand by the diazo substrate. Upon extensive experiments, it was found that the problem could be solved simply by changing the reaction concentration. Thus, when we decreased the reaction concentration from 0.2 to 0.1 M, the yield was significantly improved (entry 5). Then, the

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Scheme 1. Synthesis of Alkenylphosphonates through Palladium Carbene Coupling

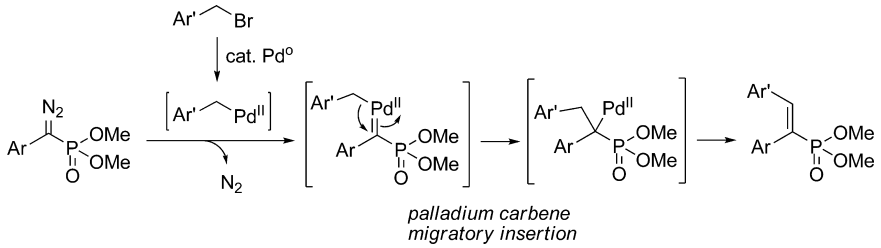
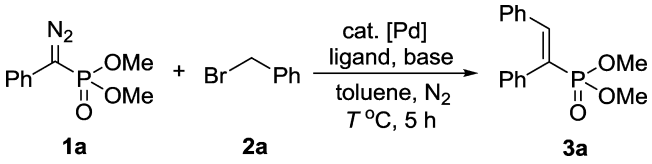


Table 1. Optimization of Reaction Conditions[a]



entry	cat. (mol %)	ligand (mol %)	conc. (M)	1a:2a	T (°C)	yield (%)[b]
1	$Pd(PPh_3)_4$ (5)	–	0.2	1:1	90	12
2	Pd_2dba_3 (2.5)	P(2-furyl)$_3$ (20)	0.2	1:1	90	16
3	$Pd(OAc)_2$ (5)	P(2-furyl)$_3$ (20)	0.2	1:1	90	24
4[c]	$Pd(OAc)_2$ (5)	P(2-furyl)$_3$ (20)	0.2	1:1	90	16
5	$Pd(OAc)_2$ (5)	P(2-furyl)$_3$ (20)	0.1	1:1	90	66
6	$Pd(OAc)_2$ (5)	P(2-furyl)$_3$ (20)	0.1	1:1	100	64
7	$Pd(OAc)_2$ (5)	P(2-furyl)$_3$ (20)	0.1	1:1	80	78
8	$Pd(OAc)_2$ (5)	P(2-furyl)$_3$ (20)	0.1	1.25:1	80	79
9	$Pd(OAc)_2$ (5)	P(2-furyl)$_3$ (20)	0.1	1:1.25	80	88
10	–	–	0.1	1:1.25	80	0

[a]The reaction was carried out with **1a** (0.2 mmol) under an atmosphere of nitrogen for 5 h. $(i\text{-Pr})_2NH$ (0.4 mmol) was used as base. [b]Isolated yields. [c]1,4-Dioxane was used as solvent.

reaction temperature was examined and the reaction was found to proceed more efficiently at 80 °C (entries 5−7). Further improvement was observed by adjusting the ratio of substrates and the reaction with 1.25 equiv of benzyl bromide was proved to afford the optimal result (entry 9). Finally, control experiment showed that no desired product could be detected in the absence of palladium catalyst (entry 10).

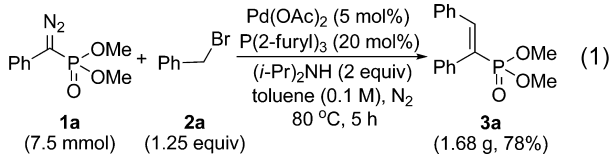
With the optimized reaction conditions established, the scope of benzyl halides was next examined. As shown in Scheme 2, the benzyl bromides bearing various functional groups proceeded well to afford the corresponding products with *E* stereoselectivity. Notably, chloro substituents are tolerated under the reaction conditions (**3d**, **3h**), which is beneficial as starting compounds for further coupling reactions. Besides, the relatively bulky methyl substituent at the *ortho* position did not hamper the reaction (**3j**). For polycyclic substrates, the reaction also went smoothly to give the corresponding alkenylphosphonates (**3k**, **3l**) in excellent yields. Gratifyingly, benzyl chlorides showed good reactivity under the same reaction conditions (**3b**, **3f**, **3l**).

Subsequently, a series of α-diazo arylmethylphosphonates were subjected to the reaction conditions (Scheme 3). The substrates bearing electron-donating groups (**1b−d**) and halogen substituents (**1e−g**) were found to undergo the desired transformation to afford the corresponding alkenylphosphonates in good yields. We observed that the diazo compounds bearing electron-withdrawing groups showed a slightly reduced reactivity because they are more reluctant to undergo dediazoniation to generate palladium carbene intermediate. Notably, α-diazo arylmethylphosphonates containing *N*-tosyl protected indole moiety was also successfully converted into the corresponding product.

Since we have previously reported the palladium-catalyzed cross-coupling of allyl halides with diazo compounds to afford 1,3-diene products,[12b] we thus conceived that the similar coupling reaction should also be extended to the reaction with α-diazo arylmethylphosphonates. As we expected, the coupling of α-diazo arylmethylphosphonates with both allyl bromides and allyl chloride proceeded well to give the corresponding 1,3-diene products in moderate to good yields under the same reaction conditions, as shown in Scheme 4.

Furthermore, we turned our attention to the synthesis of α-substituted vinylphosphonates by the coupling reaction of aryl bromides and α-diazo alkylphosphonates. However, α-diazo alkylphosphonates are not stable enough under conventional conditions for their preparation and purification, so we chose their precursor *N*-tosylhydrazones as the substrates in the coupling reaction.[11,9c] The corresponding diazo substrates are formed in situ under basic conditions. With slight modification of the standard reaction conditions, we could obtain the coupling product **9a** in 80% yield (Scheme 5). Then, a series of aryl bromides and *N*-tosylhydrazones were investigated. Aryl bromides bearing electron-donating and -withdrawing groups all proceeded well to give the desired coupling products in good yields. Various functional groups are tolerated under the reaction conditions. Moreover, substrates containing polycyclic aromatic rings and heterocycles also showed good reactivity in this transformation.

Finally, to illustrate the practical use of this synthetic method, a scale-up experiment was conducted. To our delight, the corresponding coupling product could be obtained in gram scale without significant effect in the yield (eq 1).



(1)

The high stereoselectivity for (*E*)-olefin formation can be rationalized by the transition state which is required for *syn* β-H elimination process from the alkylpalladium intermediate generated from Pd carbene migratory (Scheme 6). We propose that the aryl group Ar′ is preferred to eclipse with the less sterically bulky Ar group rather than the bulky phosphonate group, leading to (*E*)-olefin as the only product in most cases.

CONCLUSION

In summary, we have developed a highly efficient Pd-catalyzed cross-coupling reaction with α-diazo phosphonates as the

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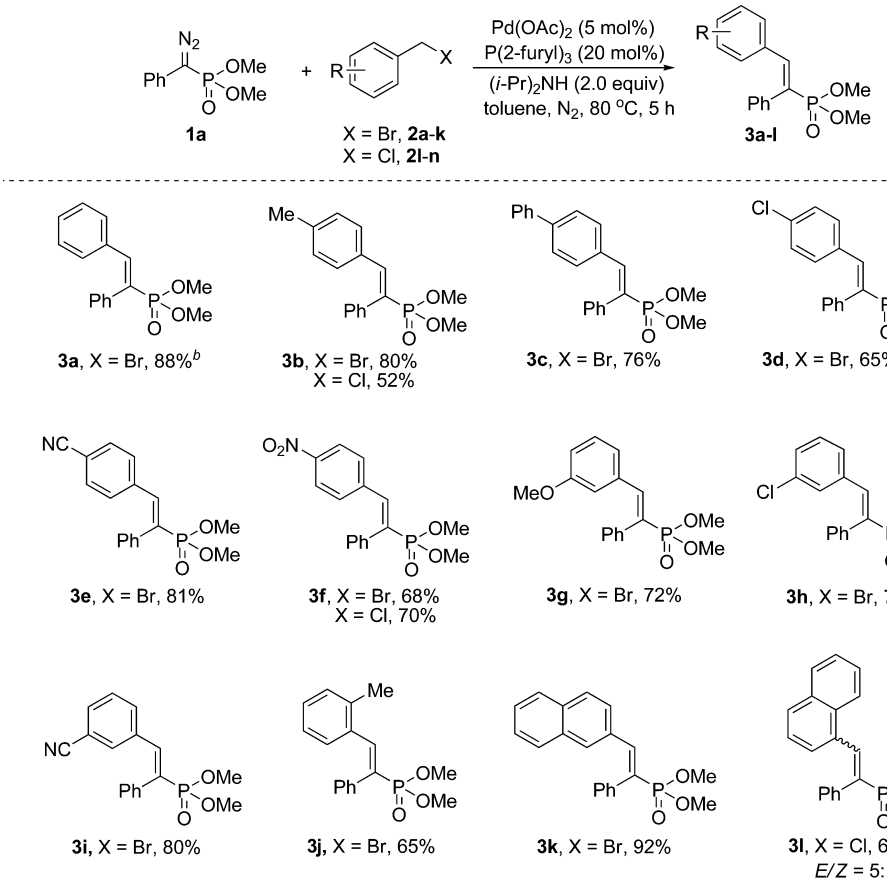
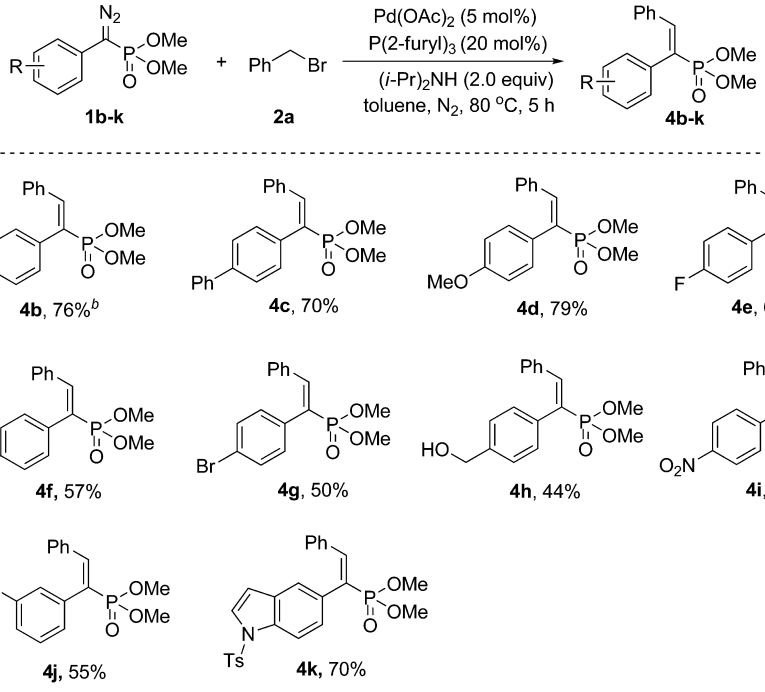
Scheme 2. Substrate Scope of Benzyl Halides[a]



[a]The reaction conditions are as following: **1a** (0.2 mmol), benzyl halides **2a-n** (0.25 mmol), toluene (2.0 mL). [b]Isolated yield. [c]*E*/*Z* ratio was determined by crude ^{1}H NMR.

Scheme 3. Substrate Scope of α-Diazo Arylmethylphosphonates[a]



[a]The reaction conditions are as following: α-diazo arylmethylphosphonates **1b−k** (0.2 mmol), benzyl bromide **2a** (0.25 mmol), toluene (2.0 mL). [b]Isolated yield.

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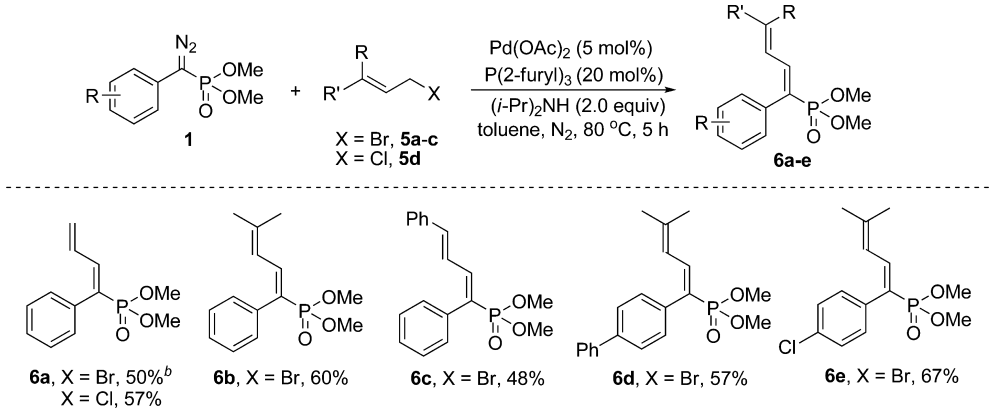
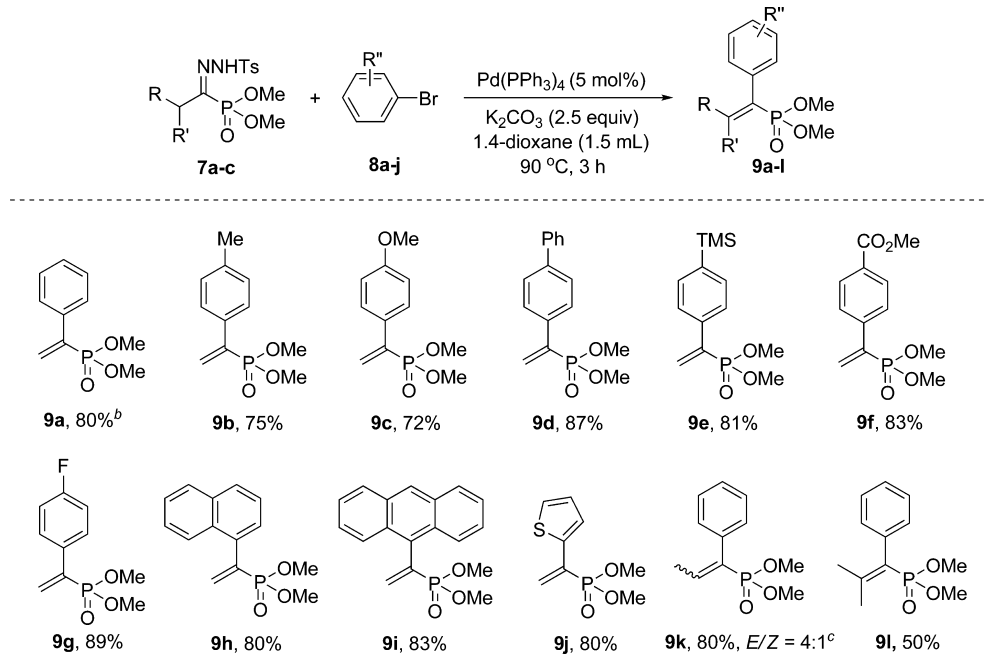
Scheme 4. Substrate Scope of Allyl Halides[a]



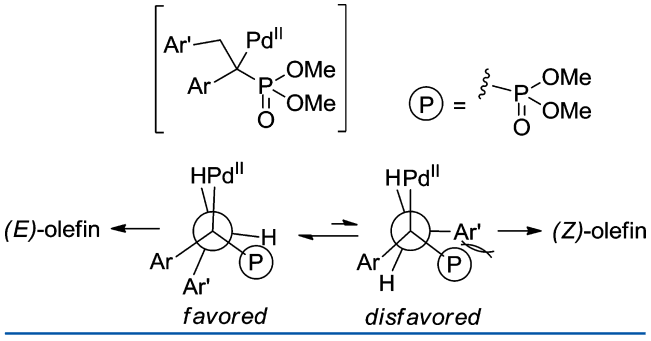
[a]The reaction conditions are as following: α-diazo arylmethylphosphonates **1** (0.2 mmol), allyl halides **5a-d** (0.25 mmol), toluene (2.0 mL). [b]Isolated yield.

Scheme 5. Reaction of *N*-Tosylhydrazones with Aryl Bromides[a]



[a]The reaction conditions are as following: *N*-tosylhydrazones **7a-c** (0.2 mmol), aryl bromides **8a-j** (0.3 mmol), 1,4-dioxane (1.5 mL). [b]Isolated yield. [c]*E*/*Z* ratio was determined by crude ^{1}H NMR.

Scheme 6. Rationalization of the Stereoselectivity



coupling partners, which constitutes a novel strategy to synthesize alkenylphosphonates. This transformation uses easily accessible reagents as the starting materials, and could efficiently produce *E*-trisubstituted alkenes bearing versatile functional groups. Further efforts concerning the application of α-diazo phosphonates in the synthesis of organophosphonate compounds are underway in our group, and the results will be reported in due course.

EXPERIMENTAL SECTION

The solvents were all distilled prior to use. MeCN, DCE and toluene were distilled from calcium hydride. Dioxane was dried over Na with benzophenone ketyl intermediate as the indicator. 200−300 mesh silica gels for the chromatography (Qingdao, China) were used. Chemical shifts for ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were reported in ppm using tetramethylsilane (TMS) as the internal standard. IR spectra are reported in wave numbers, cm^{-1}. For HRMS measurements, the mass analyzer is FT-ICR. *p*-ABSA: *p*-acetamidobenzenesulfonyl azide.

General Procedure for the Preparation of α-Diazo Arylmethylphosphonates 1a−k.[13f] The diazo compounds **1a−k** were prepared according to our previously reported method of

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palladium-catalyzed cross-coupling of dimethyl (1-diazo-2-oxopropyl)-phosphonate with aryl iodide. The dimethyl (1-diazo-2-oxopropyl)-phosphonate was prepared following a literature procedure.[14] A solution of dimethyl 2-oxopropylphosphonate (3.32 g, 20.0 mmol) in toluene (85 mL) and THF (18 mL) was stirred and cooled to 0 °C by ice−water bath for 30 min, and sodium hydride (60% in oil, 0.88 g, 22.0 mmol) was slowly added into the flask. The mixture was stirred at 0 °C under N_2 for 1 h, and *p*-ABSA (5.28 g, 22.0 mmol) was then added. The reaction was warmed to room temperature and stirring was continued overnight under N_2. The mixture was filtered through a Celite pad, and the filtrate was evaporated in vacuo to remove the volatile materials. The crude residue was purified by chromatography (silica gel, petroleum ether:ethyl acetate = 1:1) to give the product as a yellow oil (2.38 g, 62%).

$Pd(PPh_3)_4$ (116 mg, 5 mol %), K_2CO_3 (552 mg, 4.0 mmol) and aryl iodide (2.0 mmol) were suspended in methanol (5 mL) and toluene (5 mL) in a 25 mL flask under ambient atmosphere. Dimethyl (1-diazo-2-oxopropyl)phosphonate (499 mg, 1.3 equiv) was then added, and the resulting solution was stirred at room temperature for 5 h. The mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated in vacuo to remove the volatile materials. The crude residue was purified by column chromatography (silica gel, petroleum ether:EtOAc = 1:1) to afford the final products.

Dimethyl (Diazo(phenyl)methyl)phosphonate (**1a**).[13f] Orange oil, yield 80% (360 mg). R_f = 0.45 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.38 (m, 2H), 7.13−7.17 (m, 3H), 3.81 (d, J = 11.9 Hz, 6H).

Dimethyl (Diazo(p-tolyl)methyl)phosphonate (**1b**).[18] Orange oil, yield 72% (346 mg). R_f = 0.45 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 3.80 (d, J = 11.6 Hz, 6H), 2.33 (s, 3H).

Dimethyl ([1,1′-Biphenyl]-4-yl(diazo)methyl)phosphonate (**1c**). Orange oil, yield 80% (483 mg). R_f = 0.45 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.57 (d, J = 7.6 Hz, 2H), 7.42−7.45 (m, 2H), 7.32−7.36 (m, 1H), 7.23 (d, J = 8.4 Hz, 2H), 3.84 (d, J = 12.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 138.1, 128.8, 127.9, 127.3, 126.7, 125.2 (d, J = 9.5 Hz), 122.9 (d, J = 5.5 Hz), 53.2 (d, J = 5.1 Hz); IR (film) 2081, 1299, 1261, 1024, 839, 764 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{15}N_2NaO_3P$ [(M + Na)$^+$] 325.0713, found 325.0712.

Dimethyl (Diazo(4-Methoxyphenyl)methyl)phosphonate (**1d**).[18] Orange oil, yield 58% (297 mg). R_f = 0.45 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09−7.12 (m, 2H), 6.92−6.94 (m, 2H), 3.81 (d, J = 12.0 Hz, 6H), 3.80 (s, 3H).

Dimethyl (Diazo(4-fluorophenyl)methyl)phosphonate (**1e**).[13f] Orange oil, yield 50% (244 mg). R_f = 0.45 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12−7.16 (m, 2H), 7.05−7.09 (m, 2H), 3.82 (d, J = 11.9 Hz, 6H).

Dimethyl ((4-Chlorophenyl)(diazo)methyl)phosphonate (**1f**). Orange oil, yield 70% (365 mg). R_f = 0.45 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.34 (m, 2H), 7.08−7.11 (m, 2H), 3.82 (d, J = 12.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.0, 128.5, 124.0 (d, J = 9.5 Hz), 122.8 (d, J = 5.5 Hz), 52.2 (d, J = 5.1 Hz); IR (film) 2085, 1494, 1279, 1262, 1187, 1026, 837, 800 cm^{-1}; HRMS (ESI) calcd for $C_9H_{10}ClN_2NaO_3P$ [(M + Na)$^+$] 283.0010, found 283.0009.

Dimethyl ((4-Bromophenyl)(diazo)methyl)phosphonate (**1g**).[13f] Orange oil, yield 80% (488 mg). R_f = 0.45 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.6 Hz, 2H), 7.04 (d, J = 8.6 Hz, 2H), 3.81 (d, J = 11.9 Hz, 6H).

Dimethyl (Diazo(4-(hydroxymethyl)phenyl)methyl)phosphonate (**1h**). Orange oil, yield 48% (246 mg). R_f = 0.40 (petroleum ether:EtOAc = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 4.67 (s, 2H), 3.81 (d, J = 12.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 128.0, 125.2 (d, J = 9.5 Hz), 122.6 (d, J = 4.4 Hz), 64.5, 53.1 (d, J = 4.9 Hz); IR (film) 3425, 2082, 1297, 1259, 1187, 1024, 838 cm^{-1}; HRMS (ESI) calcd for $C_{10}H_{13}N_2NaO_4P$ [(M + Na)$^+$] 279.0505, found 279.0502.

Dimethyl (Diazo(4-nitrophenyl)methyl)phosphonate (**1i**).[13f] Orange oil, yield 80% (434 mg). R_f = 0.40 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.9 Hz, 2H), 7.29 (d, J = 8.9 Hz, 2H), 3.86 (d, J = 11.9 Hz, 6H).

Dimethyl (Diazo(3-methoxyphenyl)methyl)phosphonate (**1j**).[13f] Orange oil, yield 58% (297 mg). R_f = 0.45 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, J = 7.9 Hz, 1H), 6.75 (d, J = 8.2 Hz, 1H), 6.68−6.71 (m, 2H), 3.81 (d, J = 11.9 Hz, 6H), 3.80 (s, 3H).

Dimethyl (Diazo(1-tosyl-1H-indol-5-yl)methyl)phosphonate (**1k**). Orange oil, yield 61% (511 mg). R_f = 0.30 (petroleum ether:EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 3.6 Hz, 1H), 7.34 (d, J = 1.6 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.11 (dd, J = 8.8, 2.0 Hz, 1H), 6.61 (d, J = 3.6 Hz, 1H), 3.80 (d, J = 11.6 Hz, 6H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 135.0, 132.7, 131.7, 129.9, 127.2, 126.7, 121.2 (d, J = 9.6 Hz), 119.6 (d, J = 4.9 Hz), 115.5 (d, J = 4.2 Hz), 114.4, 108.7, 53.1 (d, J = 5.0 Hz), 21.5; IR (film) 2082, 1460, 1262, 1188, 1176, 1134, 1024, 735 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}N_3NaO_5PS$ [(M + Na)$^+$] 442.0597, found 442.0598.

General Procedure for the Palladium-Catalyzed Coupling Reaction of α-Diazo Arylmethylphosphonates and Benzyl or Allyl Halides. $Pd(OAc)_2$ (2.2 mg, 5 mol %), P(2-furyl)$_3$ (9.3 mg, 20 mol %), dimethyl (diazo(phenyl)methyl) phosphonate (0.20 mmol) and benzyl or allyl halide (0.25 mmol) were suspended in toluene (2 mL) in a 10 mL Schlenk tube under a nitrogen atmosphere. $(i\text{-Pr})_2NH$ (40.4 mg, 0.40 mmol) was then added, and the resulting solution was stirred at 80 °C for 5 h. The mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated in vacuo to remove the volatile materials. The crude residue was purified via preparative thin-layer chromatography (SiO_2, petroleum ether:EtOAc = 2:3) to give the final products.

Dimethyl (E)-(1,2-Diphenylvinyl)phosphonate (**3a**). Colorless oil, yield 88% (51 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 24.4 Hz, 1H), 7.35−7.37 (m, 3H), 7.24−7.26 (m, 2H), 7.13−7.20 (m, 3H), 7.05 (d, J = 7.2 Hz, 2H), 3.74 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4 (d, J = 11.1 Hz), 135.3 (d, J = 7.6 Hz), 134.5 (d, J = 22.6 Hz), 130.3 (d, J = 1.0 Hz), 129.8 (d, J = 178.6 Hz), 129.1, 129.1 (d, J = 5.4 Hz), 128.9 (d, J = 1.4 Hz), 128.2, 127.9 (d, J = 2.4 Hz), 52.7 (d, J = 5.8 Hz); IR (film) 1738, 1249, 1053, 1026, 832, 772, 719, 696 cm^{-1}; EI-MS (m/z, relative intensity) 288 (35), 192 (10), 178 (100), 152 (7); HRMS (ESI) calcd for $C_{16}H_{17}KO_3P$ [(M + K)$^+$] 327.0547, found 327.0545.

Dimethyl (E)-(1-Phenyl-2-(p-tolyl)vinyl)phosphonate (**3b**). Colorless oil, yield 80% (48 mg) for benzyl bromide and 52% (31 mg) for benzyl chloride. R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 24.8 Hz, 1H), 7.35−7.37 (m, 3H), 7.24−7.27 (m, 2H), 6.95 (m, 4H), 3.74 (d, J = 10.8 Hz, 6H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (d, J = 11.1 Hz), 139.5, 135.6 (d, J = 7.8 Hz), 131.7 (d, J = 22.8 Hz), 130.4, 129.1 (d, J = 5.4 Hz), 129.0, 128.5 (d, J = 179.5 Hz), 127.9 (d, J = 2.2 Hz), 52.7 (d, J = 5.7 Hz), 21.3 (one peak is missing because of overlap); IR (film) 1248, 1056, 1029, 910,827, 732, 699 cm^{-1}; EI-MS (m/z, relative intensity) 302 (40), 207 (12), 192 (100), 178 (11), 165 (8), 115 (6); HRMS (ESI) calcd for $C_{17}H_{20}O_3P$ [(M + H)$^+$] 303.1145, found 303.1141.

Dimethyl (E)-(2-([1,1′-Biphenyl]-4-yl)-1-phenylvinyl)phosphonate (**3c**). Colorless oil, yield 76% (55 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 24.4 Hz, 1H), 7.51−7.53 (m, 2H), 7.38−7.41 (m, 7H), 7.26−7.34 (m, 3H), 7.12 (d, J = 8.4 Hz, 2H), 3.76 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.0 (d, J = 11.2 Hz), 141.7, 140.0, 135.5 (d, J = 7.4 Hz), 133.4 (d, J = 22.9 Hz), 130.9, 129.6 (d, J = 178.9 Hz), 129.1, 129.0 (br), 128.8, 128.0 (d, J = 2.5 Hz), 127.6, 126.9, 126.8, 52.7 (d, J = 5.8 Hz); IR (film) 1249, 1055, 1028, 837, 765, 733, 698 cm^{-1}; EI-MS (m/z, relative intensity) 364 (37), 254 (100), 239 (6), 207 (11); HRMS (ESI) calcd for $C_{22}H_{22}O_3P$ [(M + H)$^+$] 365.1301, found 365.1300.

Dimethyl (E)-(2-(4-Chlorophenyl)-1-phenylvinyl)phosphonate (**3d**). Colorless oil, yield 65% (42 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 24.4 Hz, 1H), 7.36−7.38 (m, 3H), 7.22−7.24 (m, 2H), 7.11−7.13 (m, 2H),

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6.96−6.98 (m, 2H), 3.74 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0 (d, J = 11.2 Hz), 135.0, 134.9, 132.9 (d, J = 22.8 Hz), 131.5, 130.5 (d, J = 178.9 Hz), 129.0 (d, J = 1.7 Hz), 128.9 (d, J = 5.3 Hz), 128.4, 128.1 (d, J = 2.3 Hz), 52.8 (d, J = 5.8 Hz); IR (film) 1490, 1249, 1057, 1030, 911,832, 730, 700 cm^{-1}; EI-MS (m/z, relative intensity) 322 (37), 227 (5), 212 (100), 176 (22), 151 (9); HRMS (ESI) calcd for $C_{16}H_{17}ClO_3P$ [(M + H)$^+$] 323.0598, found 323.0597.

*Dimethyl (E)-(2-(4-Cyanophenyl)-1-phenylvinyl)phosphonate (**3e**).* Colorless oil, yield 81% (51 mg). R_f = 0.25 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 24.4 Hz, 1H), 7.43−7.45 (m, 2H), 7.37−7.39 (m, 3H), 7.19−7.23 (m, 2H), 7.13 (d, J = 8.4 Hz, 2H), 3.76 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (d, J = 11.2 Hz), 138.9 (d, J = 22.7 Hz), 134.3 (d, J = 7.2 Hz), 134.0 (d, J = 177.8 Hz), 131.8, 130.5, 129.1 (d, J = 1.4 Hz), 128.7 (d, J = 5.4 Hz), 128.4 (d, J = 2.2 Hz), 118.3, 112.1, 52.9 (d, J = 5.9 Hz); IR (film) 2229, 1250, 1055, 1027, 913, 836, 731, 700 cm^{-1}; EI-MS (m/z, relative intensity) 313 (60), 280 (11), 217 (17), 203 (100), 176 (15), 110 (21); HRMS (ESI) calcd for $C_{17}H_{17}NO_3P$ [(M + H)$^+$] 314.0941, found 314.0937.

*Dimethyl (E)-(2-(4-Nitrophenyl)-1-phenylvinyl)phosphonate (**3f**).* Colorless oil, yield 68% (45 mg) for benzyl bromide and 70% (47 mg) for benzyl chloride. R_f = 0.25 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−8.02 (m, 2H), 7.68 (d, J = 24.0 Hz, 1H), 7.38−7.39 (m, 3H), 7.18−7.24 (m, 4H), 3.77 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 141.3 (d, J = 11.3 Hz), 140.9 (d, J = 22.7 Hz), 134.7 (d, J = 177.6 Hz), 134.3 (d, J = 7.2 Hz), 130.8, 129.2 (d, J = 1.5 Hz), 128.7 (d, J = 5.2 Hz), 128.6 (d, J = 2.2 Hz), 123.4, 53.0 (d, J = 5.9 Hz); IR (film) 1521, 1346, 1252, 1056, 1028, 827, 733, 701 cm^{-1}; EI-MS (m/z, relative intensity) 333 (100), 316 (43), 223 (60), 207 (35), 176 (63), 110 (50); HRMS (ESI) calcd for $C_{16}H_{17}NO_5P$ [(M + H)$^+$] 334.0839, found 334.0838.

*Dimethyl (E)-(2-(3-Methoxyphenyl)-1-phenylvinyl)phosphonate (**3g**).* Colorless oil, yield 72% (46 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 24.4 Hz, 1H), 7.33−7.40 (m, 3H), 7.25−7.28 (m, 2H), 7.10 (t, J = 8.0 Hz, 1H), 6.72−6.77 (m, 2H), 6.52 (m, 1H), 3.65 (d, J = 11.2 Hz, 6H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 144.3 (d, J = 11.1 Hz), 135.6 (d, J = 22.8 Hz), 135.4, 129.8 (d, J = 178.4 Hz), 129.2, 129.1 (d, J = 5.2 Hz), 128.9 (d, J = 1.5 Hz), 127.9 (d, J = 2.2 Hz), 123.4, 116.1, 114.1, 54.7, 52.7 (d, J = 5.8 Hz); IR (film) 1246, 1051, 1027, 827, 787, 730, 699 cm^{-1}; EI-MS (m/z, relative intensity) 318 (44), 222 (7), 208 (100), 178 (14), 165 (25); HRMS (ESI) calcd for $C_{17}H_{20}O_4P$ [(M + H)$^+$] 319.1094, found 319.1092.

*Dimethyl (E)-(2-(3-Chlorophenyl)-1-phenylvinyl)phosphonate (**3h**).* Colorless oil, yield 73% (47 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 24.4 Hz, 1H), 7.37−7.38 (m, 3H), 7.22−7.25 (m, 2H), 7.16−7.18 (m, 1H), 7.07 (t, J = 8.0 Hz, 1H), 7.01 (m, 1H), 6.92 (d, J = 8.0 Hz, 1H), 3.75 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (d, J = 11.4 Hz), 136.2 (d, J = 22.9 Hz), 134.7 (d, J = 7.5 Hz), 134.0, 131.6 (d, J = 178.4 Hz), 130.1, 129.3, 129.0 (d, J = 1.7 Hz), 129.0, 128.8 (d, J = 5.2 Hz), 128.3, 128.2 (d, J = 2.2 Hz), 52.8 (d, J = 5.8 Hz); IR (film) 1247, 1057, 1030, 909, 830, 730, 700, 652 cm^{-1}; EI-MS (m/z, relative intensity) 322 (50), 226 (11), 212 (100), 196 (10), 176 (32), 151 (11); HRMS (ESI) calcd for $C_{16}H_{17}ClO_3P$ [(M + H)$^+$] 323.0598, found 323.0597.

*Dimethyl (E)-(2-(3-Cyanophenyl)-1-phenylvinyl)phosphonate (**3i**).* Colorless oil, yield 80% (50 mg). R_f = 0.25 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 24.4 Hz, 1H), 7.46−7.49 (m, 1H), 7.38−7.39 (m, 3H), 7.27−7.29 (m, 3H), 7.21−7.23 (m, 2H), 3.76 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3 (d, J = 11.4 Hz), 135.7 (d, J = 22.8 Hz), 134.2, 134.1 (br), 133.3, 133.2 (d, J = 178.3 Hz), 132.0, 129.1 (d, J = 1.3 Hz), 129.0, 128.6 (d, J = 5.2 Hz), 128.5 (d, J = 2.5 Hz), 118.0, 112.4, 52.8 (d, J = 5.9 Hz); IR (film) 2232, 1249, 1054, 1026, 829, 729, 700, 687 cm^{-1}; EI-MS (m/z, relative intensity) 312 (73), 280 (15), 217 (20), 203 (100), 176 (18), 110 (30); HRMS (ESI) calcd for $C_{17}H_{17}NO_3P$ [(M + H)$^+$] 314.0941, found 314.0938.

*Dimethyl (E)-(1-Phenyl-2-(o-tolyl)vinyl)phosphonate (**3j**).* Colorless oil, yield 65% (39 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 24.4 Hz, 1H), 7.24−7.27 (m, 3H), 7.18−7.20 (m, 2H), 7.08−7.14 (m, 2H), 6.82−6.86 (m, 1H), 6.76 (d, J = 8.0 Hz, 1H), 3.76 (d, J = 11.2 Hz, 6H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7 (d, J = 10.7 Hz), 137.4, 135.1 (d, J = 9.2 Hz), 134.0 (d, J = 21.2 Hz), 130.8 (d, J = 177.9 Hz), 130.0, 129.5 (d, J = 2.3 Hz), 129.4 (d, J = 5.6 Hz), 125.3, 128.6, 128.5, 127.7 (d, J = 2.0 Hz), 52.8 (d, J = 5.8 Hz), 20.0; IR (film) 1248, 1057, 1030, 910, 731, 698 cm^{-1}; EI-MS (m/z, relative intensity) 302 (13), 207 (23), 192 (100), 178 (15), 165 (13), 115 (12); HRMS (ESI) calcd for $C_{17}H_{20}O_3P$ [(M + H)$^+$] 303.1145, found 303.1142.

*Dimethyl (E)-(2-(Naphthalen-2-yl)-1-phenylvinyl)phosphonate (**3k**).* Colorless oil, yield 92% (62 mg). R_f = 0.35 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 24.4 Hz, 1H), 7.71−7.72 (m, 1H), 7.63−7.65 (m, 2H), 7.53 (d, J = 8.4 Hz, 1H), 7.40−7.46 (m, 2H), 7.36−7.39 (m, 3H), 7.28−7.31 (m, 2H), 7.01 (dd, J = 8.4, 1.6 Hz, 1H), 3.77 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4 (d, J = 11.1 Hz), 135.4 (d, J = 7.6 Hz), 133.2, 132.8, 132.1 (d, J = 22.7 Hz), 131.3, 129.8 (d, J = 178.8 Hz), 129.2 (d, J = 5.2 Hz), 128.9 (d, J = 1.6 Hz), 128.4, 128.0 (d, J = 2.2 Hz), 127.5, 127.4, 127.0, 126.6 (d, J = 1.0 Hz), 126.2, 52.7 (d, J = 5.8 Hz); IR (film) 1248, 1056, 1028, 910, 827, 789, 731, 699 cm^{-1}; EI-MS (m/z, relative intensity) 338 (34), 228 (100), 207 (15); HRMS (ESI) calcd for $C_{20}H_{20}O_3P$ [(M + H)$^+$] 339.1145, found 339.1143.

*Dimethyl (2-(Naphthalen-1-yl)-1-phenylvinyl)phosphonate (**3l**).* Colorless oil, yield 65% (44 mg), E/Z = 5:1. E/Z isomers are hard to separate. NMR data of the mixture were given. R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 24.0 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.81−7.87 (m, 1.6H), 7.64−7.71 (m, 2.2H), 7.48−7.56 (m, 2.6H), 7.34−7.38 (m, 0.5H), 7.11−7.19 (m, 6.2H), 7.00 (d, J = 7.2 Hz, 1H), 3.81 (d, J = 10.8 Hz, 6H), 3.57 (d, J = 10.8 Hz, 0.6H), 3.42 (d, J = 10.4 Hz, 0.6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2 (d, J = 5.2 Hz), 143.1 (d, J = 10.9 Hz), 134.9 (d, J = 9.0 Hz), 133.3, 133.2, 132.0, 131.7, 131.4, 129.5, 129.3 (d, J = 5.5 Hz), 129.2, 128.8, 128.6, 128.5, 128.4, 128.2 (d, J = 5.1 Hz), 128.1 (d, J = 2.9 Hz), 127.8 (d, J = 2.6 Hz), 127.6 (d, J = 1.9 Hz), 126.9 (d, J = 3.4 Hz), 126.7, 126.5, 126.0, 125.7, 124.9, 124.2, 124.0, 122.1, 121.4, 111.3 (d, J = 8.3 Hz), 54.0 (d, J = 7.0 Hz), 53.4 (d, J = 7.2 Hz), 52.8 (d, J = 5.8 Hz); IR (film) 1737, 1245, 1054, 1027, 829, 781, 733, 699 cm^{-1}; EI-MS (m/z, relative intensity) 338 (20), 228 (100), 202 (5); HRMS (ESI) calcd for $C_{20}H_{20}O_3P$ [(M + H)$^+$] 339.1145, found 339.1144.

*Dimethyl (E)-(2-Phenyl-1-(p-tolyl)vinyl)phosphonate (**4b**).* Colorless oil, yield 76% (46 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 24.8 Hz, 1H), 7.15−7.20 (m, 7H), 7.08 (d, J = 7.2 Hz, 2H), 3.73 (d, J = 10.8 Hz, 6H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ144.2 (d, J = 11.4 Hz), 137.6 (d, J = 2.5 Hz), 134.5 (d, J = 22.6 Hz), 132.1 (d, J = 7.7 Hz), 130.3, 129.6 (d, J = 1.4 Hz), 129.6 (d, J = 178.3 Hz), 129.0, 128.8 (d, J = 5.3 Hz), 128.1, 52.6 (d, J = 5.7 Hz), 21.2; IR (film) 1247, 1056, 1028, 837, 760, 729 cm^{-1}; EI-MS (m/z, relative intensity) 302 (45), 269 (8), 207 (19), 192 (100), 178 (15), 165 (13); HRMS (ESI) calcd for $C_{17}H_{20}O_3P$ [(M + H)$^+$] 303.1145, found 303.1141.

*Dimethyl (E)-(1-([1,1′-Biphenyl]-4-yl)-2-phenylvinyl)phosphonate (**4c**).* Colorless oil, yield 70% (51 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60−7.72 (m, 5H), 7.43−7.46 (m, 2H), 7.32−7.35 (m, 3H), 7.11−7.21 (m, 5H), 3.77 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5 (d, J = 11.0 Hz), 140.5 (d, J = 2.6 Hz), 140.3, 134.4 (d, J = 22.4 Hz), 134.2 (d, J = 7.6 Hz), 130.3, 129.5 (d, J = 5.5 Hz), 129.3 (d, J = 178.8 Hz), 129.1, 128.7, 128.2, 127.5 (d, J = 1.7 Hz), 127.4, 126.9, 52.7 (d, J = 5.8 Hz); IR (film) 1249, 1054, 1026, 821, 751, 732, 696 cm^{-1}; EI-MS (m/z, relative intensity) 364 (48), 331 (6), 254 (100), 239 (8), 207 (23); HRMS (ESI) calcd for $C_{22}H_{22}O_3P$ [(M + H)$^+$] 365.1301, found 365.1301.

*Dimethyl (E)-(1-(4-Methoxyphenyl)-2-phenylvinyl)phosphonate (**4d**).* Colorless oil, yield 79% (50 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 24.4 Hz, 1H), 7.14−7.20 (m, 5H), 7.08−7.10 (m, 2H), 6.89−6.91 (m, 2H), 3.82 (s, 3H), 3.74 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, J = 2.2 Hz), 144.2 (d, J = 11.8 Hz), 134.6 (d, J = 22.6 Hz), 130.2, 130.1 (d, J = 5.4 Hz), 129.2 (d, J = 178.8 Hz), 129.0, 128.1, 127.1 (d, J = 7.9 Hz) 114.4 (d, J = 1.3 Hz), 55.1, 52.6 (d, J = 5.8 Hz); IR (film) 1510, 1247, 1055, 1028, 828, 760 cm^{-1}; EI-MS

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(m/z, relative intensity) 318 (58), 208 (100), 193 (17), 165 (30); HRMS (ESI) calcd for $C_{17}H_{20}O_4P$ [(M + H)$^+$] 319.1094, found 319.1092.

*Dimethyl (E)-(1-(4-Fluorophenyl)-2-phenylvinyl)phosphonate (**4e**).* Colorless oil, yield 62% (38 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 24.4 Hz, 1H), 7.15−7.25 (m, 5H), 7.04−7.08 (m, 4H), 3.75 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (dd, J_{C-F} = 245.9 Hz, J_{C-P} = 2.5 Hz), 144.8 (d, J_{C-P} = 11.2 Hz), 134.2 (d, J_{C-P} = 22.4 Hz), 131.1 (dd, J_{C-F} = 3.6 Hz, J_{C-P} = 8.0 Hz), 130.9 (dd, J_{C-F} = 8.0 Hz, J_{C-P} = 5.3 Hz), 130.2, 129.2, 128.7 (d, J_{C-P} = 180.4 Hz), 128.2, 116.0 (dd, J_{C-F} = 21.6 Hz, J_{C-P} = 1.5 Hz), 52.7 (d, J_{C-P} = 5.9 Hz); IR (film) 1508, 1246, 1056, 1029, 846, 760, 730 cm^{-1}; EI-MS (m/z, relative intensity) 306 (34), 210 (6), 196 (100), 170 (5); HRMS (ESI) calcd for $C_{16}H_{17}FO_3P$ [(M + H)$^+$] 307.0894, found 307.0892.

*Dimethyl (E)-(1-(4-Chlorophenyl)-2-phenylvinyl)phosphonate (**4f**).* Colorless oil, yield 57% (38 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 24.4 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.16−7.21 (m, 5H), 7.06 (d, J = 8.0 Hz, 2H), 3.74 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8 (d, J = 10.9 Hz), 134.1 (d, J = 22.4 Hz), 133.9 (d, J = 2.9 Hz), 133.8 (d, J = 8.0 Hz), 130.5 (d, J = 5.2 Hz), 130.2, 129.3, 129.2 (d, J = 1.1 Hz), 128.5 (d, J = 180.4 Hz), 128.3, 52.7 (d, J = 5.8 Hz); IR (film) 1490, 1251, 1092, 1054, 1026, 761, 744, 694 cm^{-1}; EI-MS (m/z, relative intensity) 322 (38), 226 (6), 212 (100), 176 (21), 151 (8); HRMS (ESI) calcd for $C_{16}H_{17}ClO_3P$ [(M + H)$^+$] 323.0598, found 323.0597.

*Dimethyl (E)-(1-(4-Bromophenyl)-2-phenylvinyl)phosphonate (**4g**).* Colorless oil, yield 50% (37 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 24.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 2H), 7.12−7.22 (m, 5H), 7.06−7.08 (m, 2H), 3.75 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8 (d, J = 10.8 Hz), 134.3 (d, J = 8.0 Hz), 134.1 (d, J = 22.2 Hz), 132.2 (d, J = 1.4 Hz), 130.9 (d, J = 5.3 Hz), 130.3, 129.3, 128.6 (d, J = 180.7 Hz), 128.4, 122.2 (d, J = 3.0 Hz), 52.8 (d, J = 5.8 Hz); IR (film) 1251, 1058, 1029, 839, 735 cm^{-1}; EI-MS (m/z, relative intensity) 368 (42), 256 (100), 207 (26), 192 (15), 176 (42), 151 (14); HRMS (ESI) calcd for $C_{16}H_{17}BrO_3P$ [(M + H)$^+$] 367.0093, found 367.0095.

*Dimethyl (E)-(1-(4-(Hydroxymethyl)phenyl)-2-phenylvinyl)-phosphonate (**4h**).* Colorless oil, yield 44% (26 mg). R_f = 0.20 (petroleum ether:EtOAc = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 24.8 Hz, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.24−7.26 (m, 2H), 7.13−7.21 (m, 3H), 7.06−7.08 (m, 2H), 4.74 (s, 2H), 3.74 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6 (d, J = 11.0 Hz), 140.7 (d, J = 2.7 Hz), 134.5 (d, J = 7.8 Hz), 134.4 (d, J = 22.7 Hz), 130.3, 129.4 (d, J = 179.2 Hz), 129.2 (d, J = 5.3 Hz), 129.2, 128.2, 127.4 (d, J = 1.5 Hz), 64.9, 52.7 (d, J = 5.8 Hz); IR (film) 1236, 1056, 1028, 831, 762, 673 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{20}O_4P$ [(M + H)$^+$] 319.1094, found 319.1092.

*Dimethyl (E)-(1-(4-Nitrophenyl)-2-phenylvinyl)phosphonate (**4i**).* Colorless oil, yield 50% (33 mg). R_f = 0.25 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 24.4 Hz, 1H), 7.44−7.46 (m, 2H), 7.20−7.27 (m, 3H), 7.30 (d, J = 7.6 Hz, 2H), 3.78 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.4 (d, J = 1.9 Hz), 145.8 (d, J = 9.6 Hz), 142.8 (d, J = 7.9 Hz), 133.6 (d, J = 21.5 Hz), 130.4 (d, J = 5.1 Hz), 130.2, 129.8, 128.5, 128.1 (d, J = 181.6 Hz), 124.1, 52.9 (d, J = 5.8 Hz); IR (film) 1521, 1348, 1251, 1055, 1029, 910, 827, 789, 731, 699 cm^{-1}; EI-MS (m/z, relative intensity) 333 (100), 223 (65), 207 (51), 176 (48), 165 (32), 110 (55); HRMS (ESI) calcd for $C_{16}H_{17}NO_5P$ [(M + H)$^+$] 334.0839, found 334.0838.

*Dimethyl (E)-(1-(3-Methoxyphenyl)-2-phenylvinyl)phosphonate (**4j**).* Colorless oil, yield 55% (35 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 24.8 Hz, 1H), 7.28−7.30 (m, 1H), 7.17−7.21 (m, 3H), 7.08−7.10 (m, 2H), 6.87−6.90 (m, 1H), 6.81−6.84 (m, 2H), 3.76 (s, 3H), 3.75 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, J = 1.3 Hz), 144.4 (d, J = 11.1 Hz), 136.6 (d, J = 7.8 Hz), 134.4 (d, J = 22.5 Hz), 130.3, 129.9 (d, J = 1.5 Hz), 129.4 (d, J = 176.5 Hz), 129.1, 128.2, 121.3 (d, J = 5.6 Hz), 114.5 (d, J = 5.1 Hz), 113.4 (d, J = 2.2 Hz), 55.1, 52.7 (d, J = 5.8 Hz); IR (film) 1240, 1053, 1029, 909, 826, 758, 733 cm^{-1}; EI-MS (m/z, relative intensity) 318 (55), 285 (8), 208 (100), 178 (16), 165 (32), 139 (5); HRMS (ESI) calcd for $C_{17}H_{20}O_4P$ [(M + H)$^+$] 319.1094, found 319.1092.

*Dimethyl (E)-(2-Phenyl-1-(1-tosyl-1H-indol-5-yl)vinyl)-phosphonate (**4k**).* Colorless oil, yield 70% (67 mg). R_f = 0.30 (petroleum ether:EtOAc = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.98 (dd, J = 8.4, 0.4 Hz, 1H), 7.77−7.79 (m, 2H), 7.64 (d, J = 24.4 Hz, 1H), 7.57 (d, J = 3.6 Hz, 1H), 7.45−7.46 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.15−7.19 (m, 2H), 7.04−7.08 (m, 2H), 6.95 (d, J = 7.6 Hz, 1H), 6.54 (dd, J = 3.6, 0.4 Hz, 1H), 3.65 (d, J = 10.8 Hz, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.6 (d, J = 11.5 Hz), 135.1, 134.3 (d, J = 22.5 Hz), 134.3 (d, J = 2.0 Hz), 131.2, 130.3, 130.1 (d, J = 8.0 Hz), 129.8, 129.4 (d, J = 179.4 Hz), 129.1, 128.1, 126.8, 126.7, 125.7 (d, J = 5.4 Hz), 121.8 (d, J = 5.4 Hz), 114.1, 109.1, 52.7 (d, J = 5.8 Hz), 21.5; IR (film) 1372, 1246, 1173, 1139, 1126, 1054, 1028, 911, 833, 761, 733, 674 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}NO_5PS$ [(M + H)$^+$] 482.1186, found 482.1181.

*Dimethyl (E)-(1-Phenylbuta-1,3-dien-1-yl)phosphonate (**6a**).* Colorless oil, yield 50% (24 mg) for allyl bromide and yield 57% (27 mg) for allyl chloride. R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.40 (m, 6H), 6.31−6.41 (m, 1H), 5.62−5.67 (m, 1H), 5.41−5.44 (m, 1H), 3.72 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0 (d, J = 10.2 Hz), 134.5 (d, J = 8.7 Hz), 132.4 (d, J = 21.1 Hz), 130.1 (d, J = 181.0 Hz), 129.3 (d, J = 5.5 Hz), 128.4, 127.9 (d, J = 1.9 Hz), 125.7, 52.6 (d, J = 5.8 Hz); IR (film) 1252, 1057, 1030, 910, 830, 733, 702 cm^{-1}; EI-MS (m/z, relative intensity) 237 (100), 205 (45), 128 (81), 109 (10); HRMS (ESI) calcd for $C_{12}H_{16}O_3P$ [(M + H)$^+$] 239.0832, found 239.0829.

*Dimethyl (E)-(4-Methyl-1-phenylpenta-1,3-dien-1-yl)-phosphonate (**6b**).* Colorless oil, yield 60% (32 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, J = 22.4, 11.6 Hz), 7.39−7.31 (m, 3H), 7.25−7.23 (m, 2H), 5.84−5.87 (m, 1H), 3.70 (d, J = 11.2 Hz, 6H), 1.93 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 141.2 (d, J = 11.0 Hz), 135.1 (d, J = 9.2 Hz), 129.5 (d, J = 5.5 Hz), 128.2, 127.4 (d, J = 1.8 Hz), 125.6 (d, J = 183.5 Hz), 121.1 (d, J = 20.8 Hz), 52.4 (d, J = 5.6 Hz), 26.6, 19.0; IR (film) 1248, 1056, 1027, 912, 826, 784, 731, 699 cm^{-1}; EI-MS (m/z, relative intensity) 266 (38), 251 (19), 219 (9), 156 (100), 141 (30), 128 (11), 115 (22); HRMS (ESI) calcd for $C_{14}H_{20}O_3P$ [(M + H)$^+$] 267.1145, found 267.1142.

*Dimethyl ((1E,3E)-1,4-Diphenylbuta-1,3-dien-1-yl)phosphonate (**6c**).* Colorless oil, yield 48% (30 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.25 (m, 11H), 6.96 (d, J = 15.6 Hz, 1H), 6.81−6.74 (m, 1H), 3.73 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ144.8 (d, J = 10.5 Hz), 140.5, 136.1 (d, J = 1.9 Hz), 134.9 (d, J = 8.8 Hz), 129.5 (d, J = 5.5 Hz), 128.9 (d, J = 182.0 Hz), 128.9, 128.6, 128.4, 127.9 (d, J = 1.9 Hz), 127.2, 123.8 (d, J = 21.3 Hz), 52.5 (d, J = 5.5 Hz); IR (film) 1246, 1055, 1028, 967, 912, 827, 779, 764, 733, 700 cm^{-1}; EI-MS (m/z, relative intensity) 314 (35), 281 (6), 237 (40), 204 (100), 189 (6); HRMS (ESI) calcd for $C_{18}H_{20}O_3P$ [(M + H)$^+$] 315.1145, found 315.1142.

*Dimethyl (E)-(1-([1,1′-Biphenyl]-4-yl)-4-methylpenta-1,3-dien-1-yl)phosphonate (**6d**).* Colorless oil, yield 57% (39 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.63 (m, 5H), 7.43−7.46 (m, 2H), 7.32−7.37 (m, 3H), 5.94 (d, J = 12.0 Hz, 1H), 3.73 (d, J = 10.8 Hz, 6H), 1.95 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 141.3 (d, J = 11.0 Hz), 140.5, 140.2 (d, J = 2.1 Hz), 134.1 (d, J = 9.3 Hz), 129.9 (d, J = 5.6 Hz), 128.7, 127.3, 126.9, 125.2 (d, J = 183.3 Hz), 121.2 (d, J = 20.6 Hz), 52.4 (d, J = 5.5 Hz), 26.7, 19.0 (One peak is missing because of overlap.); IR (film) 1633, 1490, 1248, 1092, 1057, 1028, 910, 826, 732 cm^{-1}; EI-MS (m/z, relative intensity) 342 (43), 327 (50), 232 (100), 217 (25), 202 (18), 191 (15); HRMS (ESI) calcd for $C_{20}H_{24}O_3P$ [(M + H)$^+$] 343.1458, found 343.1457.

*Dimethyl (E)-(1-(4-Chlorophenyl)-4-methylpenta-1,3-dien-1-yl)-phosphonate (**6e**).* Colorless oil, yield 67% (40 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J = 22.4, 11.6 Hz, 1H), 7.33−7.35 (m, 2H), 7.17−7.20 (m, 2H), 5.80−5.83 (m, 1H), 3.70 (d, J = 10.8 Hz, 6H), 1.94 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 141.5 (d, J = 10.7 Hz),

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133.6 (d, J = 9.5 Hz), 133.4 (d, J = 2.4 Hz), 130.9 (d, J = 5.5 Hz), 128.5, 124.4 (d, J = 185.0 Hz), 120.9 (d, J = 20.8 Hz), 52.4 (d, J = 5.6 Hz), 26.7, 19.0; IR (film) 1633, 1487, 1248, 1056, 1027, 823, 732 cm^{-1}; EI-MS (m/z, relative intensity) 300 (35), 285 (10), 190 (100), 175 (11), 155 (29); HRMS (ESI) calcd for $C_{14}H_{19}ClO_3P$ $[(M + H)^+]$ 301.0755, found 301.0752.

General Procedure for the Preparation of α-Ketoalkylphosphonate *N*-Tosylhydrazones. α-Ketoalkylphosphonate *N*-tosylhydrazones **7a–c** are prepared based on the previously reported procedure.[19] A solution of pure $TsNNH_2$ (20 mmol) in 20 mL of THF in a 50 mL flask was chilled to 0 °C and 1.8 mL of concentrated HCl was added. The resulting solution was stirred in an ice bath while 20 mmol of appropriate dimethyl α-ketoalkylphosphonate was added over a 5 min period. The mixture was stirred at room temperature for 6 h. The resulting heavy white precipitate was filtered and dried to give the final product.

*Dimethyl (1-(2-Tosylhydrazono)ethyl)phosphonate (**7a**).*[19] White solid, yield 80% (5.12 g). R_f = 0.30 (petroleum ether:EtOAc = 1:3); *E*/*Z* isomers are hard to separate. NMR data of the mixture were given. ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 3.72–3.75 (m, 6H), 2.43 (s, 3H), 2.02 (d, J = 9.6 Hz, 0.4H), 1.95 (d, J = 10.8 Hz, 2.6H); IR (film) 1234, 1171, 1058, 1045, 844, 783, 668 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{20}N_2O_5PS$ $[(M + H)^+]$ 335.0825, found 335.0823.

*Dimethyl (1-(2-Tosylhydrazono)propyl)phosphonate (**7b**).* White solid, yield 70% (4.68 g). mp 199–201 °C. R_f = 0.30 (petroleum ether:EtOAc = 1:3); ^1H NMR (400 MHz, DMSO-d_6) δ 11.46 (s, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 3.53 (d, J = 10.8 Hz, 6H), 2.34–2.43 (m, 5H), 0.97 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.7 (d, J = 212 Hz), 143.8, 135.6, 129.6, 127.3, 53.2 (d, J = 6.5 Hz), 21.3 (d, J = 20.3 Hz), 21.0, 9.3; IR (film) 1234, 1171, 1058, 1045, 844, 783, 668 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{20}N_2O_5PS$ $[(M + H)^+]$ 335.0825, found 335.0823.

*Dimethyl (2-Methyl-1-(2-tosylhydrazono)propyl)phosphonate (**7c**).*[19] White solid, yield 74% (5.15 g). R_f = 0.30 (petroleum ether:EtOAc = 1:3); ^1H NMR (400 MHz, DMSO-d_6) δ 11.48 (s, 1H), 7.73 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 3.50 (d, J = 11.2 Hz, 6H), 3.00–3.14 (m, 1H), 2.38 (s, 3H), 1.05 (d, J = 6.8 Hz, 3H).

General Procedure for the Reaction of *N*-Tosylhydrazones and Aryl Bromides. $Pd(PPh_3)_4$ (12 mg, 5 mol %), K_2CO_3 (69 mg, 0.50 mmol), *N*-tosylhydrazone (0.20 mmol) and aryl bromide (0.30 mmol) were suspended in 1,4-dioxane (1.5 mL) in a 10 mL Schlenk tube under a nitrogen atmosphere. The resulting solution was stirred at 90 °C for 3 h. The mixture was filtered through a short path of silica gel, eluting with ethyl acetate, and the filtrate was evaporated in vacuo to remove the volatile materials. The crude residue was purified by column chromatography (silica gel, petroleum ether:EtOAc = 1:1) to afford the final products.

*Dimethyl (1-Phenylvinyl)phosphonate (**9a**).*[15] Colorless oil, yield 80% (34 mg). R_f = 0.35 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 7.50–7.52 (m, 2H), 7.31–7.38 (m, 3H), 6.34 (dd, J = 22.0, 1.6 Hz, 1H), 6.19 (dd, J = 46.0, 1.2 Hz, 1H), 3.74 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4 (d, J = 174.0 Hz), 136.2 (d, J = 11.7 Hz), 132.2 (d, J = 7.8 Hz), 128.3, 128.2, 127.4 (d, J = 5.8 Hz), 52.5 (d, J = 5.8 Hz).

*Dimethyl (1-(p-Tolyl)vinyl)phosphonate (**9b**).*[16] Colorless oil, yield 75% (34 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.42 (m, 2H), 7.16–7.18 (m, 2H), 6.31 (dd, J = 22.0, 1.6 Hz, 1H), 6.18 (dd, J = 46.0, 1.6 Hz, 1H), 3.74 (d, J = 10.8 Hz, 6H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 138.2 (d, J = 174.5 Hz), 133.4 (d, J = 11.7 Hz), 131.7 (d, J = 8.1 Hz), 129.2, 127.2 (d, J = 5.8 Hz), 52.6 (d, J = 5.6 Hz), 21.1.

*Dimethyl (1-(4-Methoxyphenyl)vinyl)phosphonate (**9c**).* Colorless oil, yield 72% (35 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46–7.48 (m, 2H), 6.88–6.90 (m, 2H), 6.26 (dd, J = 22.0, 1.6 Hz, 1H), 6.14 (dd, J = 46.4, 1.6 Hz, 1H), 3.82, 3.75 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 137.6 (d, J = 173.5 Hz), 130.8 (d, J = 8.2 Hz), 128.6 (d, J = 12.8 Hz), 128.5 (d, J = 6.0 Hz), 113.9, 55.2, 52.6 (d, J = 5.7 Hz); IR (film) 1512, 1252, 1183, 1031, 839, 800, 732 cm^{-1}; EI-MS (m/z, relative intensity) 242 (88), 227 (100), 195 (7), 183 (20), 167 (18); HRMS (ESI) calcd for $C_{11}H_{16}O_4P$ $[(M + H)^+]$ 243.0781, found 243.0780.

*Dimethyl (1-([1,1′-Biphenyl]-4-yl)vinyl)phosphonate (**9d**).* Colorless oil, yield 87% (51 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.61 (m, 6H), 7.43–7.46 (m, 2H), 7.31–7.36 (m, 1H), 6.37 (dd, J = 22.0, 1.2 Hz, 1H), 6.26 (dd, J = 46.0, 1.2 Hz, 1H), 3.78 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.2, 140.3, 138.0 (d, J = 173.7 Hz), 135.2 (d, J = 11.8 Hz), 132.2 (d, J = 7.9 Hz), 128.8, 127.7 (d, J = 5.8 Hz), 127.5, 127.2, 127.0, 52.7 (d, J = 5.6 Hz); IR (film) 1238, 1028,, 858, 830, 774, 743 cm^{-1}; EI-MS (m/z, relative intensity) 288 (97), 258 (10), 191 (30), 178 (100), 167 (10), 152 (19); HRMS (ESI) calcd for $C_{16}H_{18}O_3P$ $[(M + H)^+]$ 289.0988, found 289.0988.

*Dimethyl (1-(4-(Trimethylsilyl)phenyl)vinyl)phosphonate (**9e**).* Colorless oil, yield 81% (46 mg). R_f = 0.35 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.53 (m, 4H), 6.36 (dd, J = 22.4, 1.6 Hz, 1H), 6.22 (dd, J = 46.0, 1.6 Hz, 1H), 3.75 (d, J = 11.2 Hz, 6H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 138.5 (d, J = 173.6 Hz), 136.6 (d, J = 11.5 Hz), 133.5, 132.6 (d, J = 7.9 Hz), 126.5 (d, J = 5.7 Hz), 52.6 (d, J = 5.6 Hz), −1.3; IR (film) 1250, 1054, 1029, 910, 856, 835, 732 cm^{-1}; EI-MS (m/z, relative intensity) 284 (15), 269 (100), 159 (9); HRMS (ESI) calcd for $C_{13}H_{22}O_3PSi$ $[(M + H)^+]$ 285.1070, found 285.1069.

*Methyl 4-(1-(Dimethoxyphosphoryl)vinyl)benzoate (**9f**).* Colorless oil, yield 83% (45 mg). R_f = 0.25 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02–8.04 (m, 2H), 7.57–7.60 (m, 2H), 6.43 (dd, J = 22.0, 1.2 Hz, 1H), 6.19 (dd, J = 45.6, 1.2 Hz, 1H), 3.93 (s, 3H), 3.76 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 140.9 (d, J = 11.7 Hz), 138.1 (d, J = 175.6 Hz), 133.6 (d, J = 7.4 Hz), 129.9, 129.7, 127.4 (d, J = 5.7 Hz), 52.8 (d, J = 5.8 Hz), 52.1; IR (film) 1724, 1283, 1237, 1116, 1028, 830, 732 cm^{-1}; EI-MS (m/z, relative intensity) 270 (100), 239 (45), 210 (28), 102 (45), 93 (48); HRMS (ESI) calcd for $C_{12}H_{16}O_5P$ $[(M + H)^+]$ 271.0730, found 271.0730.

*Dimethyl (1-(4-Fluorophenyl)vinyl)phosphonate (**9g**).* Colorless oil, yield 89% (47 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48–7.52 (m, 2H), 7.03–7.07 (m, 2H), 6.32 (dd, J = 22.0, 1.2 Hz, 1H), 6.16 (dd, J = 46.0, 1.2 Hz, 1H), 3.76 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8 (J_{C-F} = 247.7 Hz), 137.6 (d, J_{C-P} = 175.3 Hz), 132.4 (dd, J_{C-F} = 3.2 Hz, J_{C-P} = 11.9 Hz), 132.1 (d, J_{C-P} = 8.2 Hz), 129.2 (dd, J_{C-F} = 8.1 Hz, J_{C-P} = 5.8 Hz), 115.4 (J_{C-F} = 21.4 Hz), 52.7 (d, J_{C-P} = 5.8 Hz); IR (film) 1509, 1237, 1029, 844, 832, 812, 731 cm^{-1}; EI-MS (m/z, relative intensity) 230 (96), 135 (60), 121 (100), 110 (30), 101 (80); HRMS (ESI) calcd for $C_{10}H_{13}FO_3P$ $[(M + H)^+]$ 231.0581, found 231.0581.

*Dimethyl (1-(Naphthalen-1-yl)vinyl)phosphonate (**9h**).* Colorless oil, yield 86% (45 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98–8.00 (m, 1H), 7.81–7.87 (m, 2H), 7.40–7.50 (m, 4H), 6.70 (dd, J = 22.8, 2.0 Hz, 1H), 6.06 (dd, J = 47.6, 2.0 Hz, 1H), 3.68 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8 (d, J = 176.2 Hz), 135.4 (d, J = 8.0 Hz), 134.2 (d, J = 9.4 Hz), 133.7, 131.4 (d, J = 5.1 Hz), 128.3 (d, J = 2.5 Hz), 128.2, 126.3 (d, J = 4.8 Hz), 126.2, 125.9, 125.4, 124.9 (d, J = 2.2 Hz), 52.9 (d, J = 6.0 Hz); IR (film) 1253, 1236, 1055, 1030, 833, 813, 780, 734 cm^{-1}; EI-MS (m/z, relative intensity) 262 (12), 229 (5), 152 (100); HRMS (ESI) calcd for $C_{14}H_{16}O_3P$ $[(M + H)^+]$ 263.0832, found 263.0832.

*Dimethyl (1-(Anthracen-9-yl)vinyl)phosphonate (**9i**).* Colorless oil, yield 83% (52 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^1H NMR (400 MHz, $CDCl_3$) δ 8.43–8.44 (m, 1H), 8.08–8.11 (m, 2H), 7.97–7.99 (m, 2H), 7.44–7.50 (m, 2H), 6.94 (dd, J = 22.4, 2.0 Hz, 1H), 6.09 (dd, J = 48.0, 2.0 Hz, 1H), 3.57 (d, J = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8 (d, J = 178.2 Hz), 136.3 (d, J = 7.5 Hz), 131.2 (d, J = 2.4 Hz), 130.7 (d, J = 7.3 Hz), 129.8 (d, J = 4.8 Hz), 128.3, 127.5 (d, J = 3.6 Hz), 126.3 (d, J = 2.0 Hz), 125.6, 125.2, 52.9 (d, J = 6.5 Hz); IR (film) 1252, 1057, 1032, 831, 785, 741 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}O_3P$ $[(M + H)^+]$ 313.0988, found 313.0987.

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*Dimethyl (1-(Thiophen-2-yl)vinyl)phosphonate (**9j**).* Colorless oil, yield 76% (33 mg). R_f = 0.30 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dt, J = 4.0, 1.2 Hz, 1H), 7.26 (dt, J = 5.2, 1.2 Hz, 1H), 7.01 (dd, J = 4.8, 3.6 Hz, 1H), 6.28 (d, J = 44.4 Hz, 1H), 6.20 (d, J = 21.2 Hz, 1H), 3.78 (d, J = 11.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6 (d, J = 16.8 Hz), 131.3 (d, J = 176.4 Hz), 129.7 (d, J = 7.1 Hz), 127.8, 127.4 (d, J = 3.3 Hz), 125.8, 52.8 (d, J = 5.4 Hz); IR (film) 1271, 1232, 1027, 854, 833, 732 cm^{-1}; EI-MS (m/z, relative intensity) 218 (41), 188 (46), 123 (15), 109 (100), 65 (28); HRMS (ESI) calcd for $C_8H_{12}O_3PS$ [(M + H)$^+$] 219.0239, found 219.0239.

*Dimethyl (E)-(1-Phenylprop-1-en-1-yl)phosphonate (**9k**).*[17] Colorless oil, yield 64% (29 mg). R_f = 0.35 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29−7.39 (m, 3H), 7.19−7.22 (m, 2H), 6.34 (dq, J = 22.8, 2.8 Hz, 1H), 3.69 (d, J = 10.8 Hz, 6H), 1.74 (dd, J = 6.8, 3.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8 (d, J = 10.2 Hz), 134.5 (d, J = 10.1 Hz), 131.4 (d, J = 180.4 Hz), 129.1 (d, J = 5.0 Hz), 128.3, 127.5 (d, J = 2.1 Hz), 52.5 (d, J = 5.9 Hz), 15.6 (d, J = 18.8 Hz).

*Dimethyl (2-Methyl-1-phenylprop-1-en-1-yl)phosphonate (**9l**).* Colorless oil, yield 50% (24 mg). R_f = 0.35 (petroleum ether:EtOAc = 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25−7.35 (m, 3H), 7.11−7.13 (m, 2H), 3.60 (d, J = 10.8 Hz, 6H), 2.31 (d, J = 3.2 Hz, 3H), 1.65 (d, J = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8 (d, J = 11.7 Hz), 138.6 (d, J = 10.5 Hz), 129.5 (d, J = 4.4 Hz), 128.2, 126.9 (d, J = 2.2 Hz), 126.0 (d, J = 181.4 Hz), 52.1 (d, J = 5.9 Hz), 24.2 (d, J = 18.3 Hz), 23.2 (d, J = 7.1 Hz); IR (film) 1235, 1057, 1031, 910, 823, 731, 703 cm^{-1}; EI-MS (m/z, relative intensity) 239 (84), 225 (10), 149 (25), 129 (100), 115 (42); HRMS (ESI) calcd for $C_{12}H_{18}O_3P$ [(M + H)$^+$] 241.0988, found 241.0987.

■ ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H and ^{13}C spectra for all products. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00629.

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Notes

The authors declare no competing financial interest.

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