Synthesis C. Wu et al. Paper

Synthesis of Allenylphosphonates through Cu(I)-Catalyzed Coupling of Terminal Alkynes with Diazophosphonates

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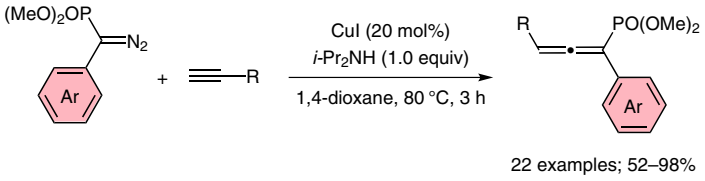

22 examples; 52–98%

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Abstract Through the Cu(I)-catalyzed coupling of diazophosphonates with terminal alkynes, an efficient method for the synthesis of allenylphosphonates has been developed. Simple and inexpensive CuI is used as the catalyst and the reaction is conducted under mild conditions.

Key words diazophosphonate, allene, cross-coupling, carbene, copper

Due to the characteristics of two perpendicular π-bonds, the chemistry of allenes has emerged as a bourgeoning research topic in organic chemistry and other related areas, such as pharmaceutical research.[1,2] Among the allene structural units that have been widely discovered in natural products and pharmaceuticals,[1,3] allenylphosphonates play an especially important role in biological and medicinal chemistry. Besides, because of the electron-withdrawing nature of the phosphonate group, allenylphosphonates are found to be potentially useful synthetic intermediates.[4] The prominent reactivity features of this type of allene compounds are: 1) selective addition of various N-, O-, and S-nucleophiles;[5–7] 2) selective total or partial hydrogenation;[8,9] 3) radical reactions;[10] and 4) Diels–Alder reaction and other cycloadditions.[11,12] In addition, a number of compounds containing allenylphosphonates show interesting biological activities.[13] For example, allene **1** shows DNA cleavage and antitumor activity[14] and G6PDH (**2**) is an inhibitor for the glucose-6-phosphate dehydrogenase[3a] (Figure 1).

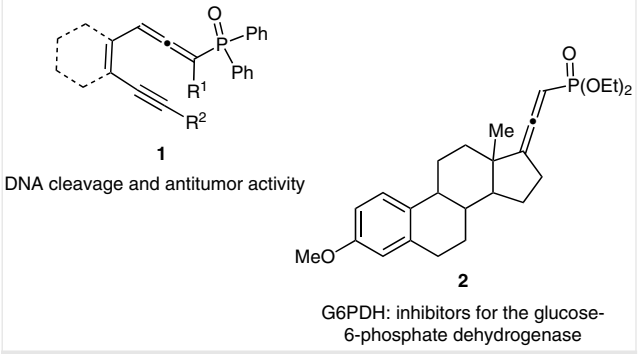
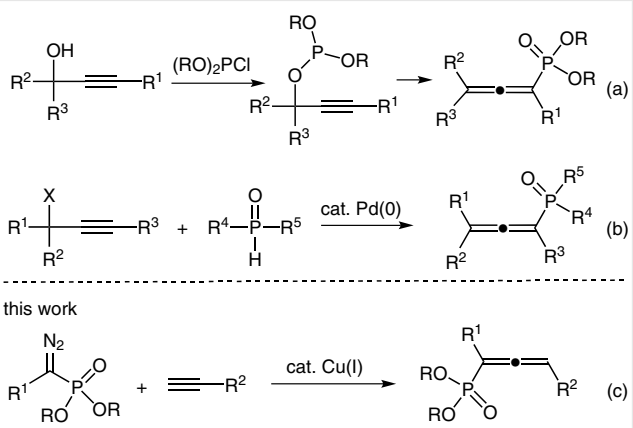


Figure 1 Biologically active allenes

On account of their wide applications in various fields, it is highly desirable to develop efficient methods for the synthesis of allenylphosphonates.

The synthetic methods for allenylphosphonates documented in the literature are summarized in Scheme 1. The first method generates allenylphosphonates via [2,3]-sigmatropic rearrangement of propargyl phosphates, which are easily obtained from the corresponding propargylic alcohols (Scheme 1, a).[15] Although the substrate scope of propargylic alcohols is wide, the corresponding phosphates that can be derived by simple nucleophilic reaction with phosphorochloridates is rather limited. The second method that has attracted significant attention in allenylphosphonate synthesis is based on the transition-metal-catalyzed propargylic substitution (S_N2') reaction (Scheme 1, b).[16] The reaction affords the allenylphosphonate products in good yields with wide substrate scope. However, the reaction requires complex ligands, and the by-products are usually not easy to separate, which significantly limits the practical application of this method.



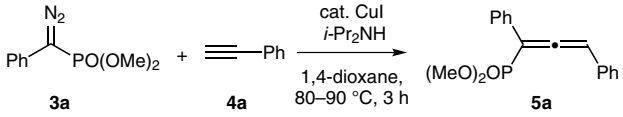
Scheme1 Synthetic strategies towards allenylphosphonates

Recently, we and others have developed a novel method for the allene synthesis based on the copper(I)-catalyzed cross-coupling of *N*-tosylhydrazones or diazo compounds with terminal alkynes.[17] In view of the importance of allenylphosphonates, we have conceived that a similar copper(I)-catalyzed cross-coupling of terminal alkynes with diazophosphonates may serve as a novel approach for the synthesis of allenylphosphonates. Herein we report our studies along these lines (Scheme 1, c).

The study began with the evaluation of the feasibility of the reaction between dimethyl [diazo(phenyl)methyl]phosphonate (**3a**) and phenylacetylene (**4a**), with CuI as the catalyst, *i*-Pr_2NH as the base, and 1,4-dioxane as the solvent (Table 1). The desired product **5a** was obtained in 72% yield at 90 °C (Table 1, entry 1). Slightly lowering the reaction temperature to 80 °C improved the yield to 82% (entry 2). The yield was further enhanced when the amount of **3a** was slightly increased (entry 3). Attempts to reduce either the catalyst loading or the amount of base led to diminished yields, although the reaction still proceeded smoothly to give moderate yields of the allene product (entries 4–6).

With the optimized reaction conditions in hand, the scope of this reaction was then explored with a series of diazophosphonates and terminal alkynes. First, the scope of terminal alkynes was examined through the reaction with diazophosphonate **3a** (Scheme 2). Under identical reaction conditions, the reactions afforded the corresponding allene products **5b**–**n** in good yields. It is noteworthy that the reactions were not significantly affected by the substituents on the aromatic ring in terminal alkynes **4b**–**i**. Moreover, the reaction also worked with terminal alkynes bearing substituents such as heterocycle **5j**, alkenyl **5k**, and alkyl **5l**, **5m**. In particular, a substrate containing an unprotected hydroxyl group was applied in the synthesis of **5m**. Interestingly, when the alkyne bearing TIPS (triisopropylsilyl) substituent was subjected to the reaction, the main product was the internal alkyne **5n′**, instead of the allene product. The ratio of alkyne **5n′** and the minor product allene **5n** was

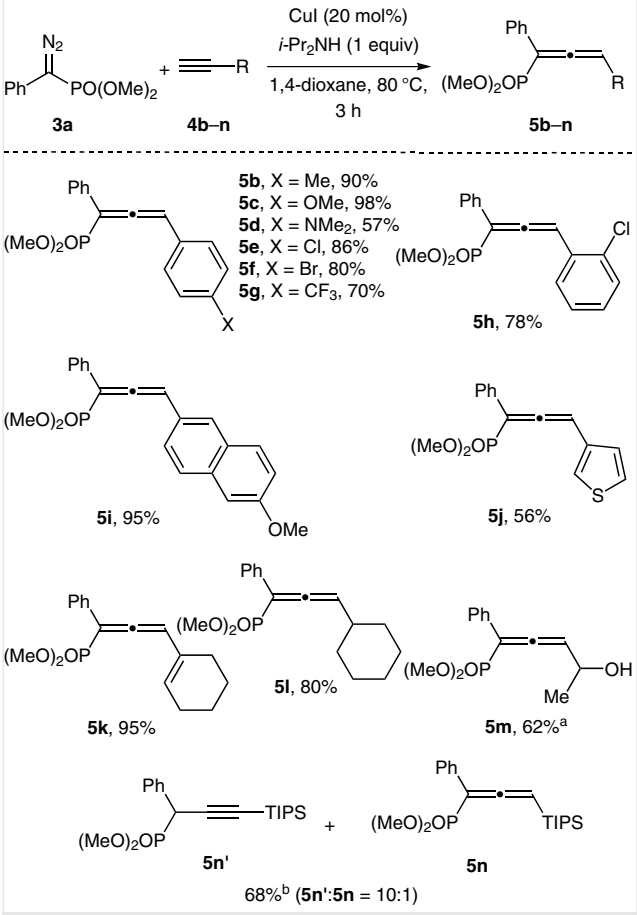
Table 1 Optimization of Reaction Conditions[a]



3a **4a** **5a**

Entry	**3a** (equiv)	Cat. (mol%)	Base (mol%)	Temp (°C)	Yield (%)[b]
1	1.2	CuI (20)	*i*-Pr_2NH (100)	90	72
2	1.2	CuI (20)	*i*-Pr_2NH (100)	80	82
3	1.3	CuI (20)	*i*-Pr_2NH (100)	80	85
4	1.3	CuI (10)	*i*-Pr_2NH (100)	80	75
5	1.3	CuI (20)	*i*-Pr_2NH (20)	80	70
6	1.3	CuI (20)	*i*-Pr_2NH (60)	80	75

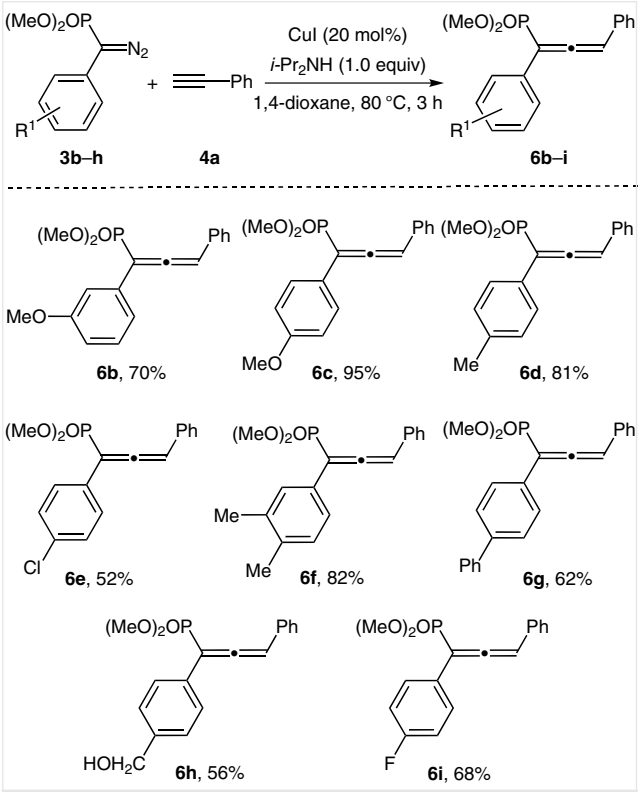
[a]Reaction conditions: **3a**, **4a** (0.2 mmol), CuI, and *i*-Pr_2NH in 1,4-dioxane (1 mL) under an N_2 atmosphere for 3 h.
[b] Isolated yields by column chromatography.



Scheme 2 The substrate scope of terminal alkynes. *Reaction conditions:* **3a** (1.3 equiv), terminal alkynes **4b**–**n** (0.2 mmol), CuI (20 mol%), *i*-Pr_2NH (1.0 equiv) in 1.4-dioxane (1 mL) under N_2 at 80 °C for 3 h; isolated yields by column chromatography. [a] Diastereomeric ratio (dr): 1:1. [b] Overall yield of **5n** and **5n′**. Ratio of **5n′**/**5n**: 10:1.

approximately 10:1. This result is consistent with our previous report on the Cu(I)-catalyzed Csp–Csp[3] cross-coupling of *N*-tosylhydrazones and trialkylsilylethynes.[18,19]

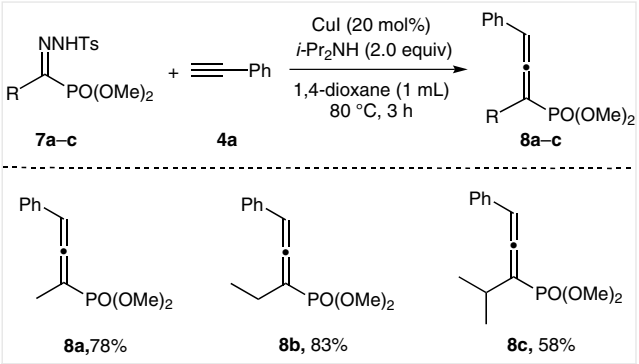
Next, the reaction scope was investigated for a variety of aryldiazophosphonates under the optimized reaction conditions (Scheme 3). The reactions examined under the identical conditions afforded the corresponding allene products in good yields. It is also noteworthy that the reactions were not significantly affected by the substituents on the aromatic ring in diazophosphonates **3b**–**i**.



Scheme 3 The substrate scope of diazophosphonates. *Reaction conditions*: diazophosphonates **3b**–**i** (1.3 equiv), **4a** (0.2 mmol), CuI (20 mol%), and *i*-Pr_2NH (1 equiv) in 1,4-dioxane (1 mL) under N_2 at 80 °C for 3 h; isolated yields by column chromatography.

Generally, diazophosphonates containing electron-donating groups gave better results than those with electron-withdrawing groups on the aromatic ring. In addition, diazophosphonate **3h** with a free hydroxyl group is also subjected to the reaction, affording the desired product **6h** in moderate yield.

Encouraged by the success in the reaction of aryldiazophosphonates, we next tried to extend the reaction scope to achieve the preparation of alkyldiazophosphonates. *N*-Tosylhydrazones **7a-c** derived from acylphosphonates were used as the starting materials; these generated the corresponding diazo compounds in situ in the presence of a base. At the beginning of our study, we employed the *N*-tosylhydrazone **7a** and phenylacetylene (**4a**) as the model substrates. Following the reaction conditions applied in our previous work,[17] we first tried to use inorganic bases, such as LiO*t*-Bu and K_2CO_3. Only a trace amount of the allene product was observed when LiO*t*-Bu was used as the base, while the yield reached 53% when K_2CO_3 was the base in the reaction system. To our delight, the desired allene product was obtained in 78% yield when *i*-Pr_2NH was used as the base. Moreover, ethyl and isopropyl groups could all be introduced into the allene products in moderate to excellent yields (Scheme 4).



Scheme 4 The scope of alkyldiazophosphonates. *Reaction conditions*: *N*-tosylhydrazones **7a**–**c** (1.2 equiv), **4a** (0.2 mmol), CuI (20 mol%) and *i*-Pr_2NH (2.0 equiv) in 1,4-dioxane (1 mL) under N_2 at 80 °C for 3 h; isolated yields by column chromatography.

In conclusion, we have developed a novel synthetic method for allenylphosphonates from terminal alkynes and diazophosphonates through the alkynyl migratory insertion into a Cu-carbene. The reaction is operationally simple providing good yields, and the conditions are mild without the need for complex ligands. It is thus expected that this reaction will find wide applications in organic synthesis and pharmaceutical research.

All reactions were performed under an N_2 atmosphere in a 10 mL Schlenk tube. 1,4-Dioxane was dried over Na before use. For chromatographic purification, 200–300 mesh silica gel (Qingdao, China) was employed. ^1H NMR and ^{13}C NMR spectra were recorded on Varian 300 MHz and Bruker ARX 400 MHz spectrometer in $CDCl_3$ or DMSO-d_6 solution and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm). Unless otherwise noted, the chemicals obtained from commercial suppliers were used without further purification.

CuI-Catalyzed Cross-Coupling of Diazophosphonates 3 with Terminal Alkynes 4; General Procedure

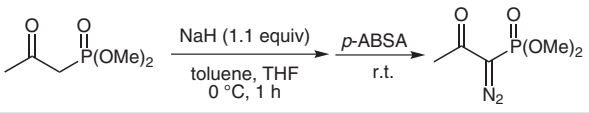
Under an N_2 atmosphere, the corresponding terminal alkyne **4** (0.2 mmol) was added to a mixture of CuI (8 mg, 0.04 mmol), *i*-Pr_2NH (20 mg, 0.2 mmol), and the appropriate diazophosphonate **3** (0.26 mmol) in 1,4-dioxane (1 mL). The solution was stirred at 80 °C for 3 h and the progress of the reaction was monitored by TLC. Upon completion of

the reaction, the reaction mixture was cooled down to r.t. and filtered through a short pad of silica gel using EtOAc as eluent. The solvent was removed in vacuo to leave a crude mixture, which was purified by column chromatography on silica gel to afford the corresponding product **5** or **6**.

CuI-Catalyzed Cross-Coupling of α-Ketoalkylphosphonate *N*-Tosylhydrazones 7 with Phenyl Acetylene (4a); General Procedure

Under an N_2 atmosphere, phenyl acetylene (**4a**; 0.2 mmol) was added to a mixture of CuI (8 mg, 0.04 mmol), *i*-Pr_2NH (40 mg, 0.4 mmol), and the appropriate α-ketoalkylphosphonate *N*-tosylhydrazone **7** (0.24 mmol) in 1,4-dioxane (1 mL). The solution was stirred at 80 °C for 3 h and the progress of the reaction was monitored by TLC. Upon completion of the reaction, the reaction mixture was cooled down to r.t. and filtered through a short pad of silica gel using EtOAc as eluent. The solvent was removed in vacuo to leave a crude mixture, which was purified by column chromatography on silica gel to afford the corresponding product **8**.

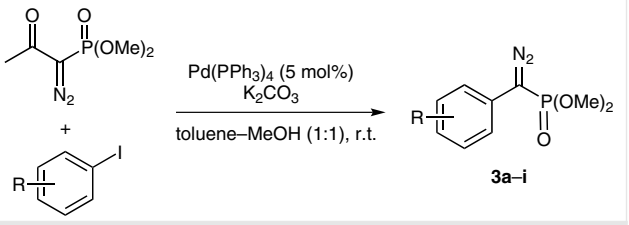
Dimethyl (1-Diazo-2-oxopropyl)phosphonate (Scheme 5)



Scheme 5

Under an N_2 atmosphere, a suspension of NaH (60% in oil, 0.88 g, 22.0 mmol) in toluene (85 mL) and THF (18 mL) was stirred and cooled to 0 °C in an ice–water bath for 30 min. To this suspension was added slowly dimethyl 2-oxopropylphosphonate (3.32 g, 20.0 mmol). The mixture was stirred at 0 °C for 1 h, and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA; 5.28 g, 22.0 mmol) was then added. The reaction was warmed to r.t. and stirring was continued overnight. 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, PE–EtOAc, 1:1) to give the product as a yellow oil; yield: 2.38 g (62%).

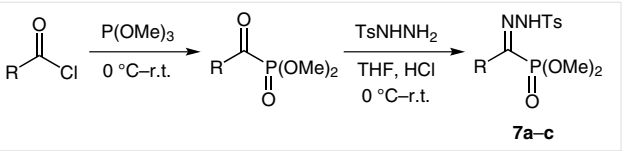
Aryldiazophosphonates 3a–i[20] (Scheme 6)



Scheme 6

Under an ambient atmosphere, $Pd(PPh_3)_4$ (116 mg, 5 mol%), K_2CO_3 (552 mg, 4.0 mmol), and the corresponding aryl iodide (2.0 mmol) were suspended in MeOH (5 mL) and toluene (5 mL) in a 25 mL flask. Dimethyl (1-diazo-2-oxopropyl)phosphonate (499 mg, 1.3 equiv) was then added, and the resulting solution was stirred at r.t. for 5 h. The mixture was filtered through a short pad of silica gel eluting with EtOAc and the filtrate was evaporated in vacuo to remove the volatile materials. The crude residue was purified by column chromatography (silica gel, EtOAc–PE, 1:1) to afford the respective final product **3**; yield: 50–90%.

α-Ketoalkylphosphonate *N*-Tosylhydrazones 7a–c;[21] General Procedure (Scheme7)



Scheme 7

Dimethylα-Ketoalky1phosphonates: Under an N_2 atmosphere, the appropriate acyl halide (20 mmol) was stirred in a flask equipped with a dropping funnel and a magnetic stirring assembly at 0 °C. $P(OMe)_3$ (2.6 g, 21 mmol, distilled before use) was added dropwise over a period of 20–60 min, depending on the reaction scale. The reaction mixture was stirred for 6 h at r.t. and the solution was used directly in the following step without further workup.

α-Ketoalkylphosphonate N-Tosylhydrazones: Under an ambient atmosphere, a solution of pure $TsNHNH_2$ (3.72 g, 20 mmol) in THF (20 mL) in a 50 mL flask was cooled to 0 °C and concd HCl (1.8 mL) was added. The resulting solution was stirred in an ice bath while the above-mentioned mixture solution was added over a 5 min period. The mixture was stirred at r.t. for 6 h. The resulting white precipitate was filtered and dried to give the final product **7**; yield: 70–80%.

Dimethyl [Diazo(phenyl)methyl]phosphonate (3a)[20a]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 360 mg (80%); yellow oil; R_f = 0.45 (EtOAc–PE, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.38 (m, 2 H), 7.13–7.17 (m, 3 H), 3.81 (d, *J* = 11.9 Hz, 6 H).

Dimethyl [Diazo(3-methoxyphenyl)methyl]phosphonate (3b)[20a]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 297 mg (58%); yellow oil; R_f = 0.45 (EtOAc–PE, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 (t, *J* = 7.9 Hz, 1 H), 6.75 (d, *J* = 8.2 Hz, 1 H), 6.68–6.71 (m, 2 H), 3.81 (d, *J* = 11.9 Hz, 6 H), 3.80 (s, 3 H).

Dimethyl [Diazo(4-methoxyphenyl)methyl]phosphonate (3c)[20a]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 297 mg (58%); yellow oil; R_f = 0.45 (EtOAc–PE, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.09–7.12 (m, 2 H), 6.92–6.94 (m, 2 H), 3.81 (d, *J* = 12.0 Hz, 6 H), 3.80 (s, 3 H).

Dimethyl [Diazo(*p*-tolyl)methyl]phosphonate (3d)[20a]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 346 mg (72%); yellow oil; R_f = 0.45 (EtOAc–PE, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.4 Hz, 2 H), 7.06 (d, *J* = 8.4 Hz, 2 H), 3.80 (d, *J* = 11.6 Hz, 6 H), 2.33 (s, 3 H).

Dimethyl [(4-Chlorophenyl)(diazo)methyl]phosphonate (3e)[20b]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 365 mg (70%); yellow oil; R_f = 0.45 (EtOAc–PE, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.34 (m, 2 H), 7.08–7.11 (m, 2 H), 3.82 (d, *J* = 12.0 Hz, 6 H).

^{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).

Dimethyl [Diazo(3,4-dimethylphenyl)methyl]phosphonate (3f)[20a]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 320 mg (65%); yellow oil; R_f = 0.45 (EtOAc–PE, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.5 Hz, 1 H), 6.92–6.90 (m, 2 H), 3.80 (d, *J* = 11.9 Hz, 6 H), 2.26 (s, 3 H), 2.24 (s, 3 H).

Dimethyl [(1,1′-Biphenyl)-4-yl(diazo)methyl]phosphonate (3g)[20b]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 301 mg (59%); yellow oil; R_f = 0.45 (EtOAc–PE, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 8.4 Hz, 2 H), 7.57 (d, *J* = 7.6 Hz, 2 H), 7.42–7.45 (m, 2 H), 7.32–7.36 (m, 1 H), 7.23 (d, *J* = 8.4 Hz, 2 H), 3.84 (d, *J* = 12.0 Hz, 6 H).

^{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).

Dimethyl {Diazo[4-(hydroxymethyl)phenyl]methyl}phosphonate (3h)[20b]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 48 mg (45%); yellow oil; R_f = 0.40 (EtOAc–PE, 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (d, *J* = 8.4 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 4.67 (s, 2 H), 3.81 (d, *J* = 12.0 Hz, 6 H).

^{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).

Dimethyl [Diazo(4-fluorophenyl)methyl]phosphonate (3i)[20a]

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 365 mg (70%); yellow oil; R_f = 0.45 (EtOAc–PE, 1:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12–7.16 (m, 2 H), 7.05–7.09 (m, 2 H), 3.82 (d, *J* = 11.9 Hz, 6 H).

Dimethyl (1,3-Diphenylpropa-1,2-dien-1-yl)phosphonate (5a)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 51 mg (85%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2952, 1930, 1598, 1493, 1251, 1208, 911, 831, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$: δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.31–7.35 (m, 6 H), 7.25–7.27 (m, 2 H), 6.76 (d, *J* = 12.4 Hz, 1 H), 3.80 (d, *J* = 11.6 Hz, 3 H), 3.77 (d, *J* = 11.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.58 (d, *J* = 2.7 Hz), 131.24 (d, *J* = 8.0 Hz), 130.96 (d, *J* = 7.7 Hz), 128.86 (d, *J* = 1.2 Hz), 128.63, 127.98, 127.48 (d, *J* = 6.0 Hz), 127.11, 127.08, 100.60 (d, *J* = 187.2 Hz), 97.95 (d, *J* = 15.2 Hz), 53.30 (d, *J* = 6.6 Hz), 53.22 (d, *J* = 6.4 Hz).

EI-MS: *m*/*z* (%) = 300 (M^+, 10), 281 (12), 263 (5), 249 (13), 239 (100), 207 (80), 191 (10), 155 (5), 117 (11), 105 (15), 91 (70).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{17}H_{18}O_3P$: 301.0988; found: 301.0991.

Dimethyl [1-Phenyl-3-(*p*-tolyl)propa-1,2-dien-1-yl]phosphonate (5b)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 57 mg (90%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2952, 1928, 1543, 1493, 1260, 1027, 830, 770 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 2 H), 7.24–7.29 (m, 3 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 6.74 (d, *J* = 12.4 Hz, 1 H), 3.80 (d, *J* = 11.2 Hz, 3 H), 3.77 (d, *J* = 10.8 Hz, 3 H), 2.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.70 (d, *J* = 2.7 Hz), 138.05 (d, *J* = 1.7 Hz), 131.20 (d, *J* = 8.1 Hz), 129.64 (d, *J* = 1.0 Hz), 128.67, 128.21 (d, *J* = 7.8 Hz), 127.96, 127.53 (d, *J* = 6.1 Hz), 127.08 (d, *J* = 2.2 Hz), 100.52 (d, *J* = 187.7 Hz), 97.80 (d, *J* = 15.3 Hz), 53.39 (d, *J* = 6.1 Hz), 53.29 (d, *J* = 6.4 Hz), 21.14.

EI-MS: *m*/*z* (%) = 314 (M^+, 49), 299 (16), 282 (6), 267 (7), 221 (5), 205 (100), 189 (12).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{18}H_{20}O_3P$: 315.1145; found: 315.1149.

Dimethyl [3-(4-Methoxyphenyl)-1-phenylpropa-1,2-dien-1-yl]phosphonate (5c)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 65 mg (98%); colorless oil; R_f = 0.40 (EtOAc–PE, 1:1).

IR (film): 2953, 1929, 1606, 1511, 1250, 1173, 1027, 831, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.5 Hz, 3 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 6.74 (d, *J* = 12.8 Hz, 1 H), 3.80 (d, *J* = 11.2 Hz, 3 H), 3.79 (s, 3 H), 3.78 (d, *J* = 11.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.71 (d, *J* = 2.7 Hz), 159.43, 131.34 (d, *J* = 8.3 Hz), 128.67, 128.41 (d, *J* = 2.4 Hz), 127.94, 127.52 (d, *J* = 6.0 Hz), 123.28 (d, *J* = 8.1 Hz), 114.45, 100.52 (d, *J* = 188.0 Hz), 97.60 (d, *J* = 15.3 Hz), 55.21, 53.37 (d, *J* = 6.1 Hz), 53.48 (d, *J* = 6.5 Hz).

EI-MS: *m*/*z* (%) = 330 (M^+, 39), 315 (25), 283 (7), 221 (100), 206 (10), 178 (20), 152 (8), 109 (5).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{18}H_{20}O_4P$: 331.1094; found: 331.1099.

Dimethyl {3-[4-(Dimethylamino)phenyl]-1-phenylpropa-1,2-dien-1-yl}phosphonate (5d)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 39 mg (57%); colorless oil; R_f = 0.40 (EtOAc–PE, 1:1).

IR (film): 2987, 1924, 1607, 1523, 1250, 1028, 831, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 8.0 Hz, 2 H), 7.22–7.35 (m, 5 H), 6.73 (d, *J* = 12.8 Hz, 1 H), 6.67–6.70 (m, 2 H), 3.80 (d, *J* = 11.2 Hz, 3 H), 3.78 (d, *J* = 11.6 Hz, 3 H), 2.96 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.33 (d, *J* = 2.8 Hz), 150.28, 131.79 (d, *J* = 9.2 Hz), 128.63, 128.24 (d, *J* = 2.2 Hz), 127.76, 127.53 (d, *J* = 6.2 Hz), 118.03 (d, *J* = 7.9 Hz), 112.57, 100.21 (d, *J* = 188.6 Hz), 98.14 (d, *J* = 15.6 Hz), 53.43 (d, *J* = 6.2 Hz), 53.31 (d, *J* = 6.6 Hz), 42.29.

EI-MS: *m*/*z* (%) = 343 (M^+, 7), 235 (100), 199 (15), 165 (58), 105 (7), 79 (3).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{19}H_{23}NO_3P$: 344.1410; found: 344.1413.

Dimethyl [3-(4-Chlorophenyl)-1-phenylpropa-1,2-dien-1-yl]phosphonate (5e)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 58 mg (86%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 1930, 1491, 1257, 1027, 831, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 2 H), 7.27–7.38 (m, 7 H), 6.73 (d, *J* = 12.8 Hz, 1 H), 3.81 (d, *J* = 11.2 Hz, 3 H), 3.78 (d, *J* = 10.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.66 (d, *J* = 2.7 Hz), 133.77 (d, *J* = 2.0 Hz), 130.75 (d, *J* = 7.6 Hz), 129.95 (d, *J* = 8.1 Hz), 129.16 (d, *J* = 1.1 Hz), 128.79, 128.35 (d, *J* = 2.3 Hz), 128.23, 127.59 (d, *J* = 5.9 Hz), 101.19 (d, *J* = 186.9 Hz), 97.16 (d, *J* = 15.3 Hz), 53.42 (d, *J* = 6.7 Hz), 53.35 (d, *J* = 6.9 Hz).

EI-MS: *m*/*z* (%) = 334 (M$^+$, 42), 319 (11), 299 (9), 287 (5), 269 (5), 237 (7), 225 (100), 189 (48), 163 (8), 109 (10).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{17}H_{17}ClO_3P$: 335.0598; found: 335.0605.

Dimethyl [3-(4-Bromophenyl)-1-phenylpropa-1,2-dien-1-yl]phosphonate (5f)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 61 mg (80%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 1930, 1487, 1256, 1027, 831, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.30–7.38 (m, 3 H), 7.21–7.23 (m, 2 H), 6.71 (d, *J* = 12.2 Hz, 1 H), 3.80 (d, *J* = 11.6 Hz, 3 H), 3.78 (d, *J* = 11.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.66 (d, *J* = 2.7 Hz), 132.14 (d, *J* = 1.1 Hz), 130.71 (d, *J* = 7.3 Hz), 130.46 (d, *J* = 8.1 Hz), 128.82, 128.67 (d, *J* = 2.5 Hz), 128.28, 127.62 (d, *J* = 6.0 Hz), 121.91 (d, *J* = 2.0 Hz), 101.28 (d, *J* = 186.9 Hz), 97.26 (d, *J* = 15.3 Hz), 53.46 (d, *J* = 6.3 Hz), 53.39 (d, *J* = 6.6 Hz).

EI-MS: *m*/*z* (%) = 378 (M$^+$, 32), 363 (5), 299 (33), 269 (100), 237 (21), 189 (85), 163 (7), 109 (11).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{17}H_{17}BrO_3P$: 379.0093; found: 379.0101.

Dimethyl {1-Phenyl-3-[4-(trifluoromethyl)phenyl]propa-1,2-dien-1-yl}phosphonate (5g)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 52 mg (70%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2959, 1931, 1616, 1324, 1259, 1166, 1123, 1064, 1027, 831, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (t, *J* = 7.6 Hz, 4 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 7.27–7.39 (m, 3 H), 6.79 (d, *J* = 12.8 Hz, 1 H), 3.83 (d, *J* = 10.8 Hz, 3 H), 3.80 (d, *J* = 10.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.97 (d, *J* = 2.6 Hz), 135.50 (d, *J* = 9.1 Hz), 130.46 (d, *J* = 7.2 Hz), 129.90 (q, *J* = 32.8 Hz), 128.88, 128.41, 127.66 (d, *J* = 3.0 Hz), 127.35 (d, *J* = 2.2 Hz), 125.95 (d, *J* = 3.1 Hz), 123.90 (q, *J* = 270.8 Hz), 101.52 (d, *J* = 186.5 Hz), 97.10 (d, *J* = 15.1 Hz), 53.47 (d, *J* = 6.0 Hz), 53.41 (d, *J* = 5.4 Hz).

EI-MS: *m*/*z* (%) = 368 (M$^+$, 50), 353 (8), 336 (7), 306 (5), 275 (5), 259 (100), 240 (25), 169 (28), 109 (21).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{18}H_{17}F_3O_3P$: 369.0862; found: 369.0869.

Dimethyl [3-(2-Chlorophenyl)-1-phenylpropa-1,2-dien-1-yl]phosphonate (5h)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 52 mg (78%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2954, 1932, 1738, 1477, 1247, 1030, 909, 833, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.0 Hz, 2 H), 7.46–7.49 (m, 1 H), 7.34–7.41 (m, 3 H), 7.28–7.32 (m, 1 H), 7.17–7.25 (m, 3 H), 3.83 (d, *J* = 11.6 Hz, 3 H), 3.79 (d, *J* = 11.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.04 (d, *J* = 2.7 Hz), 132.36 (d, *J* = 3.0 Hz), 130.59 (d, *J* = 7.4 Hz), 129.88, 129.40 (d, *J* = 7.9 Hz), 129.00 (d, *J* = 1.2 Hz), 128.68, 128.50 (d, *J* = 2.2 Hz), 128.09, 127.53 (d, *J* = 6.2 Hz), 127.07, 100.79 (d, *J* = 186.8 Hz), 94.36 (d, *J* = 15.2 Hz), 53.30 (d, *J* = 6.1 Hz).

EI-MS: *m*/*z* (%) = 334 (M$^+$, 62), 319 (12), 299 (25), 225 (100), 189 (60), 163 (5), 109 (7).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{17}H_{17}ClO_3P$: 335.0598; found: 335.0606.

Dimethyl [3-(6-Methoxynaphthalen-2-yl)-1-phenylpropa-1,2-dien-1-yl]phosphonate (5i)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 72 mg (95%); colorless oil; R_f = 0.45 (EtOAc–PE, 1:1).

IR (film): 2952, 2242, 1929, 1732, 1629, 1604, 1235, 1030, 908, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.70 (m, 5 H), 7.45–7.47 (m, 1 H), 7.37 (t, *J* = 8.0 Hz, 2 H), 7.26–7.309 (m, 1 H), 7.10–7.15 (m, 2 H), 6.81 (d, *J* = 12.4 Hz, 1 H), 3.89 (s, 3 H), 3.82 (d, *J* = 11.2 Hz, 3 H), 3.79 (d, *J* = 11.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.07 (d, *J* = 2.5 Hz), 157.95, 134.23, 131.20 (d, *J* = 8.2 Hz), 129.24, 128.92 (d, *J* = 1.3 Hz), 128.72, 128.03, 127.58 (d, *J* = 5.9 Hz), 127.27, 126.40 (d, *J* = 3.0 Hz), 126.32 (d, *J* = 8.2 Hz), 124.96 (d, *J* = 1.2 Hz), 119.20, 105.80, 100.79 (d, *J* = 187.7 Hz), 98.45 (d, *J* = 15.3 Hz), 55.18, 53.45 (d, *J* = 6.3 Hz), 53.32 (d, *J* = 6.5 Hz).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{22}H_{22}O_4P$: 381.1250; found: 381.1258.

Dimethyl (1-Phenyl-3-(thiophen-3-yl)propa-1,2-dien-1-yl]phosphonate (5j)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 34 mg (56%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2952, 1929, 1492, 1254, 1027, 827, 770, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.0 Hz, 2 H), 7.21–7.39 (m, 5 H), 7.10–7.11 (m, 1 H), 6.84 (d, *J* = 12.8 Hz, 1 H), 3.81 (d, *J* = 11.2 Hz, 3 H), 3.80 (d, *J* = 11.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 213.33 (d, *J* = 2.7 Hz), 131.91 (d, *J* = 8.2 Hz), 131.20 (d, *J* = 8.1 Hz), 128.73, 128.05, 127.64 (d, *J* = 6.0 Hz), 126.72, 126.01 (d, *J* = 1.0 Hz), 122.87 (d, *J* = 3.6 Hz), 99.91 (d, *J* = 187.5 Hz), 92.59 (d, *J* = 15.3 Hz), 53.39 (d, *J* = 6.2 Hz), 53.33 (d, *J* = 6.7 Hz).

EI-MS: *m*/*z* (%) = 306 (M^+, 30), 291 (21), 274 (7), 259 (6), 207 (25), 197 (100), 152 (12), 91 (10).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{15}H_{16}O_3PS$: 307.0552; found: 307.0557.

Dimethyl [3-(Cyclohex-2-en-1-yl)-1-phenylpropa-1,2-dien-1-yl]phosphonate (5k)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 58 mg (95%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2928, 1922, 1493, 1443, 1259, 1026, 829, 765, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.0 Hz, 2 H), 7.34 (t, *J* = 8.0 Hz, 2 H), 7.24–7.28 (m, 1 H), 6.43 (d, *J* = 12.4 Hz, 1 H), 5.48 (d, *J* = 2.4 Hz, 1 H), 3.80 (d, *J* = 11.2 Hz, 3 H), 3.78 (d, *J* = 11.2 Hz, 3 H), 2.14–2.19 (m, 4 H), 1.58–1.70 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.50 (d, *J* = 2.9 Hz), 131.89 (d, *J* = 8.6 Hz), 129.55 (d, *J* = 8.6 Hz), 129.27 (d, *J* = 5.0 Hz), 128.54, 127.64, 127.34 (d, *J* = 5.8 Hz), 101.28 (d, *J* = 15.3 Hz), 99.56 (d, *J* = 189.2 Hz), 53.13 (d, *J* = 6.4 Hz), 53.11 (d, *J* = 6.1 Hz), 25.89 (d, *J* = 2.1 Hz), 25.88, 22.18, 21.94.

EI-MS: *m*/*z* (%) = 304 (M^+, 30), 289 (5), 276 (4), 194 (100), 179 (19), 165 (30), 152 (8), 115 (18), 91 (11), 79 (7).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{17}H_{22}O_3P$: 305.1301; found: 305.1301.

Dimethyl (3-Cyclohexyl-1-phenylpropa-1,2-dien-1-yl)phosphonate (5l)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 49 mg (80%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2925, 2551, 1939, 1448, 1259, 1027, 828, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.0 Hz, 2 H), 7.33 (t, *J* = 7.6 Hz, 2 H), 7.23–7.28 (m, 1 H), 5.75 (dd, *J* = 6.0, 12.4 Hz, 1 H), 3.78 (d, *J* = 11.2 Hz, 6 H), 2.22–2.27 (m, 1 H), 1.87–1.90 (m, 2 H), 1.74–1.77 (m, 2 H), 1.66 (d, *J* = 12.4 Hz, 1 H), 1.22–1.30 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.97 (d, *J* = 4.3 Hz), 132.08 (d, *J* = 9.1 Hz), 128.52, 127.42, 127.19 (d, *J* = 6.0 Hz), 100.58 (d, *J* = 14.9 Hz), 97.1 (d, *J* = 190.2 Hz), 53.06 (d, *J* = 6.0 Hz), 53.03 (d, *J* = 5.9 Hz), 37.11 (d, *J* = 5.7 Hz), 32.88 (d, *J* = 3.0 Hz), 32.74 (d, *J* = 3.1 Hz), 25.85, 25.82, 25.79.

EI-MS: *m*/*z* (%) = 306 (M^+, 100), 277 (15), 265 (52), 237 (20), 224 (20), 196 (62), 167 (62), 153 (51), 129 (45), 115 (91), 93 (17).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{17}H_{24}O_3P$: 307.1458; found: 307.1461.

Dimethyl (4-Hydroxy-1-phenylpenta-1,2-dien-1-yl)phosphonate (5m)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 37 mg (62%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1). The diastereoisomers were difficult to separate; hence the spectral data of the diastereoisomeric mixture are given below.

IR (film): 3365, 2594, 1954, 1494, 1448, 1244, 1026, 831, 76 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (t, *J* = 8.0 Hz, 2 H), 7.34 (t, *J* = 7.2 Hz, 2 H), 7.25–7.27 (m, 1 H), 5.87–5.96 (m, 1 H), 4.57–4.60 (m, 1 H), 3.79 (d, *J* = 11.2 Hz, 3 H), 3.76 (d, *J* = 11.2 Hz, 3 H), 1.42 (d, *J* = 6.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.67 (d, *J* = 4.5 Hz), 209.45 (d, *J* = 4.5 Hz), 131.32 (d, *J* = 4.7 Hz), 131.25 (d, *J* = 4.5 Hz), 128.63, 128.60, 127.81, 127.42 (d, *J* = 5.7 Hz), 127.36 (d, *J* = 5.6 Hz), 100.63 (d, *J* = 14.4 Hz), 100.49 (d, *J* = 14.4 Hz), 98.36 (d, *J* = 187.9 Hz), 97.85 (d, *J* = 187.3 Hz), 65.51 (d, *J* = 6.0 Hz), 64.98 (d, *J* = 6.0 Hz), 53.21 (d, *J* = 6.0 Hz), 53.18 (d, *J* = 5.9 Hz), 53.13 (d, *J* = 5.3 Hz), 53.08 (d, *J* = 5.6 Hz), 23.31 (d, *J* = 2.7 Hz), 23.18 (d, *J* = 3.0 Hz).

HRMS (ESI): *m*/*z* [(M + Na)$^+$] calcd for $C_{13}H_{17}O_4PNa$: 291.0757; found: 291.0752.

Dimethyl [1-Phenyl-3-(triisopropylsilyl)prop-2-yn-1-yl]phosphonate (5n')

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 52 mg (68%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1). The two isomers were difficult to separate; hence the spectral data for the main product are given.

IR (film): 2944, 2865, 2174, 1918, 1463, 1263, 1030, 830, 679 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.54 (m, 2 H), 7.27–7.37 (m, 3 H), 4.20 (d, *J* = 28.4 Hz, 1 H), 3.72 (d, *J* = 5.2 Hz, 3 H), 3.69 (d, *J* = 5.2 Hz, 3 H), 1.11 (s, 21 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.87 (d, *J* = 8.6 Hz), 128.87 (d, *J* = 5.1 Hz), 128.42 (d, *J* = 3.0 Hz), 127.58 (d, *J* = 3.5 Hz), 100.80 (d, *J* = 13.4 Hz), 86.67 (d, *J* = 8.5 Hz), 54.36 (d, *J* = 7.0 Hz), 53.82 (d, *J* = 6.9 Hz), 38.42 (d, *J* = 137.2 Hz), 18.51, 11.21.

EI-MS: *m*/*z* (%) = 380 (M^+, 5), 337 (100), 203 (5), 181 (3), 143 (5), 91 (70).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{20}H_{34}O_3PSi$: 381.2009; found: 381.2018.

Dimethyl [1-(3-Methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl]phosphonate (6b)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 46 mg (70%); colorless oil; R_f = 0.40 (EtOAc–PE, 1:1).

IR (film): 2954, 1925, 1957, 1485, 1258, 1179, 1027, 831, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.38 (m, 4 H), 7.24–7.29 (m, 3 H), 7.13–7.22 (m, 2 H), 6.76 (d, *J* = 12.8 Hz, 1 H), 3.81 (d, *J* = 11.6 Hz, 3 H), 3.79 (s, 3 H), 3.78 (d, *J* = 11.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.83 (d, *J* = 2.9 Hz), 159.78, 132.47 (d, *J* = 7.8 Hz), 131.38 (d, *J* = 7.9 Hz), 129.74, 129.00 (d, *J* = 1.2 Hz), 128.12 (d, *J* = 1.2 Hz), 127.28 (d, *J* = 2.4 Hz), 120.16 (d, *J* = 5.9 Hz), 113.69, 113.27 (d, *J* = 6.4 Hz), 100.67 (d, *J* = 187.9 Hz), 98.09 (d, *J* = 15.3 Hz), 55.22, 53.49 (d, *J* = 6.9 Hz), 53.40 (d, *J* = 6.5 Hz).

EI-MS: *m*/*z* (%) = 330 (M^+, 53), 315 (11), 298 (7), 283 (8), 266 (7), 221 (100), 178 (21), 152 (10), 109 (7).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{18}H_{20}O_4P$: 331.1094; found: 31.1099.

Dimethyl [1-(4-Methoxyphenyl)-3-phenylpropa-1,2-dien-1-yl]phosphonate (6c)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 63 mg (95%); colorless oil; R_f = 0.40 (EtOAc–PE, 1:1).

IR (film): 2954, 1929, 1606, 1509, 1252, 1180, 1028, 834, 751 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 2 H), 7.32–7.36 (m, 4 H), 7.25–7.28 (m, 1 H), 6.88 (d, *J* = 8.8 Hz, 2 H), 6.74 (d, *J* = 12.8 Hz, 1 H), 3.80 (d, *J* = 11.2 Hz, 3 H), 3.79 (s, 3 H), 3.78 (d, *J* = 11.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.05 (d, *J* = 2.9 Hz), 159.49, 131.66 (d, *J* = 8.0 Hz), 128.93 (d, *J* = 2.2 Hz), 128.86 (d, *J* = 6.4 Hz), 127.97 (d, *J* = 3.2 Hz), 127.17 (d, *J* = 2.2 Hz), 122.98 (d, *J* = 7.9 Hz), 114.20, 100.16 (d, *J* = 187.0 Hz), 98.05 (d, *J* = 15.3 Hz), 55.21, 53.40 (d, *J* = 6.1 Hz), 53.32 (d, *J* = 6.5 Hz).

EI-MS: *m*/*z* (%) = 330 (M^+, 51), 315 (10), 283 (7), 221 (100), 206 (5), 178 (12), 152 (5).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{18}H_{20}O_4P$: 331.1094; found: 331.1099.

Dimethyl [3-Phenyl-1-(*p*-tolyl)propa-1,2-dien-1-yl]phosphonate (6d)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 51 mg (81%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2952, 1929, 1510, 1457, 1252, 1027, 830, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.0 Hz, 2 H), 7.31–7.36 (m, 4 H), 7.24–7.28 (m, 1 H), 7.15 (d, *J* = 8.4 Hz, 2 H), 6.74 (d, *J* = 12.4 Hz, 1 H), 3.80 (d, *J* = 11.2 Hz, 3 H), 3.77 (d, *J* = 11.2 Hz, 3 H), 2.34 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.41 (d, *J* = 2.7 Hz), 138.04, 131.54 (d, *J* = 8.0 Hz), 129.45, 128.92, 127.98 (d, *J* = 1.6 Hz), 127.96 (d, *J* = 6.7 Hz), 127.47 (d, *J* = 6.0 Hz), 127.19 (d, *J* = 2.3 Hz), 100.51 (d, *J* = 186.8 Hz), 97.98 (d, *J* = 15.3 Hz), 53.39 (d, *J* = 6.1 Hz), 53.31 (d, *J* = 6.3 Hz), 21.09.

EI-MS: *m*/*z* (%) = 314 (M^+, 52), 299 (11), 282 (9), 267 (7), 250 (5), 205 (100), 169 (12).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{18}H_{20}O_3P$: 315.1145; found: 315.1150.

Dimethyl [1-(4-Chlorophenyl)-3-phenylpropa-1,2-dien-1-yl]phosphonate (6e)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 35 mg (52%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2953, 1930, 1490, 1257, 1027, 835, 773 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 8.4 Hz, 2 H), 7.30–7.36 (m, 7 H), 6.78 (d, *J* = 12.8 Hz, 1 H), 3.81 (d, *J* = 11.6 Hz, 3 H), 3.78 (d, *J* = 11.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.67 (d, *J* = 2.7 Hz), 134.06, 131.05 (d, *J* = 7.6 Hz), 129.63 (d, *J* = 8.3 Hz), 129.05 (d, *J* = 1.0 Hz), 128.93, 128.75 (d, *J* = 5.9 Hz), 128.28 (d, *J* = 1.3 Hz), 127.28 (d, *J* = 2.4 Hz), 99.97 (d, *J* = 188.3 Hz), 98.46 (d, *J* = 5.0 Hz), 53.53 (d, *J* = 6.3 Hz), 53.44 (d, *J* = 6.6 Hz).

EI-MS: *m*/*z* (%) = 334 (M^+, 55), 319 (12), 302 (6), 287 (5), 225 (100), 189 (50), 163 (5), 109 (10).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{17}H_{17}ClO_3P$: 335.0598; found: 335.0606.

Dimethyl [1-(3,4-Dimethylphenyl)-3-phenylpropa-1,2-dien-1-yl]phosphonate (6f)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 54 mg (82%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2951, 1925, 1501, 1456, 1258, 1026, 831, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.39 (m, 6 H), 7.24–7.28 (m, 1 H), 7.11 (d, *J* = 8.4 Hz, 1 H), 6.73 (d, *J* = 12.8 Hz, 1 H), 3.80 (d, *J* = 11.2 Hz, 3 H), 3.78 (d, *J* = 10.8 Hz, 3 H), 2.24 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.41 (d, *J* = 3.0 Hz), 137.05, 136.83, 131.69 (d, *J* = 8.0 Hz), 130.02, 128.94 (d, *J* = 1.0 Hz), 128.64 (d, *J* = 6.3 Hz), 128.32 (d, *J* = 7.7 Hz), 127.95 (d, *J* = 1.7 Hz), 127.23 (d, *J* = 2.3 Hz), 125.08 (d, *J* = 5.9 Hz), 100.58 (d, *J* = 186.6 Hz), 97.84 (d, *J* = 15.3 Hz), 53.43 (d, *J* = 6.1 Hz), 53.33 (d, *J* = 6.4 Hz), 19.79, 19.45.

EI-MS: *m*/*z* (%) = 328 (M^+, 50), 313 (4), 286 (7), 281 (4), 264 (4), 219 (100), 202 (15), 178 (7), 109 (5).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{19}H_{22}O_3P$: 329.1301; found: 329.1307.

Dimethyl {1-[(1,1′-Biphenyl)-4-yl]-3-phenylpropa-1,2-dien-1-yl}phosphonate (6g)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 54 mg (62%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2952, 1929, 1487, 1457, 1259, 1027, 832, 767, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.4 Hz, 2 H), 7.54–7.59 (m, 4 H), 7.41–7.45 (m, 2 H), 7.32–7.39 (m, 5 H), 7.25–7.29 (m, 1 H), 6.80 (d, *J* = 12.4 Hz, 1 H), 3.84 (d, *J* = 11.2 Hz, 3 H), 3.81 (d, *J* = 11.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.89 (d, *J* = 2.6 Hz), 140.96, 140.40, 131.41 (d, *J* = 8.0 Hz), 130.01 (d, *J* = 7.9 Hz), 129.04, 128.78, 128.17 (d, *J* = 1.2 Hz), 128.05 (d, *J* = 6.0 Hz), 127.49, 127.48 (d, *J* = 2.1 Hz), 127.31 (d, *J* = 2.3 Hz), 126.98, 100.53 (d, *J* = 187.4 Hz), 98.29 (d, *J* = 15.1 Hz), 53.53 (d, *J* = 6.1 Hz), 53.44 (d, *J* = 6.5 Hz).

EI-MS: *m*/*z* (%) = 376 (M^+, 5), 357 (25), 330 (7), 281 (8), 221 (12), 207 (30), 133 (100), 105 (20), 77 (18).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{23}H_{22}O_3P$: 377.1301; found: 377.1308.

Dimethyl {1-[4-(Hydroxymethyl)phenyl]-3-phenylpropa-1,2-dien-1-yl}phosphonate (6h)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 43 mg (56%); colorless oil; R_f = 0.30 (EtOAc–PE, 1:1).

IR (film): 3401, 2958, 1929, 1716, 1457, 1247, 1028, 833, 730 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (d, *J* = 8.4 Hz, 2 H), 7.31–7.39 (m, 1 H), 7.25–7.27 (m, 5 H), 7.19–7.22 (m, 1 H), 6.68 (d, *J* = 12.8 Hz, 1 H), 4.58 (s, 2 H), 3.72 (d, *J* = 11.2 Hz, 3 H), 3.69 (d, *J* = 10.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.70 (d, *J* = 2.8 Hz), 141.26, 132.02 (d, *J* = 10.0 Hz), 131.37 (d, *J* = 8.0 Hz), 130.13 (d, *J* = 8.0 Hz), 129.01 (d, *J* = 1.1 Hz), 128.14 (d, *J* = 1.1 Hz), 127.72 (d, *J* = 6.0 Hz), 127.26, 100.45 (d, *J* = 187.8 Hz), 98.15 (d, *J* = 15.3 Hz), 64.60, 53.50 (d, *J* = 6.8 Hz), 53.28 (d, *J* = 6.9 Hz).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{18}H_{20}O_4P$: 331.1094; found: 331.1099.

Dimethyl [1-(4-Fluorophenyl)-3-phenylpropa-1,2-dien-1-yl]phosphonate (6i)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 43 mg (68%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2924, 1930, 1508, 1458, 1258, 1027, 840 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.63 (m, 2 H), 7.35 (d, *J* = 4.4 Hz, 4 H), 7.27–7.31 (m, 1 H), 7.04 (t, *J* = 8.4 Hz, 2 H), 6.77 (d, *J* = 12.4 Hz, 1 H), 3.82 (d, *J* = 11.6 Hz, 3 H), 3.78 (d, *J* = 11.6 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 212.47 (d, *J* = 2.9 Hz), 162.58 (d, *J* = 247.0 Hz), 131.27 (d, *J* = 7.9 Hz), 129.50 (d, *J* = 6.0 Hz), 129.41 (d, *J* = 6.2 Hz), 129.07 (d, *J* = 0.9 Hz), 128.25 (d, *J* = 1.5 Hz), 127.28 (d, *J* = 2.3 Hz), 115.39 (d, *J* = 21.7 Hz), 99.94 (d, *J* = 188.2 Hz), 98.31 (d, *J* = 15.2 Hz), 53.55 (d, *J* = 6.1 Hz), 53.45 (d, *J* = 6.4 Hz).

EI-MS: *m*/*z* (%) = 318 (M^+, 55), 303 (7), 286 (5), 271 (5), 254 (3), 225 (5), 209 (100), 163 (7), 109 (5).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{17}H_{17}FO_3P$: 319.0894; found: 319.6900.

Dimethyl [1-(2-Tosylhydrazono)ethyl]phosphonate (7a)[21]

Following the general procedure described above, the crude residue was purified by recrystallization; yield: 5.12 g (80%); white solid; R_f = 0.30 (EtOAc–PE, 3:1). The *E*/*Z*-isomers were difficult to separate.

^{1}H NMR (400 MHz, $CDCl_3$): δ (*E*/*Z*-mixture) = 8.72 (s, 1 H), 7.82 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 3.72–3.75 (m, 6 H), 2.43 (s, 3 H), 2.02 (d, *J* = 9.6 Hz, 0.4 H), 1.95 (d, *J* = 10.8 Hz, 2.6 H).

Dimethyl [1-(2-Tosylhydrazono)propyl]phosphonate (7b)[20b]

Following the general procedure described above, the crude residue was purified by recrystallization; yield: 4.68 g (70%); white solid; R_f = 0.30 (EtOAc–PE, 3:1).The *E*/*Z*-isomers were difficult to separate.

^{1}H NMR (400 MHz, DMSO-d_6): δ (*E*/*Z*-mixture) = 11.46 (s, 1 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 3.53 (d, *J* = 10.8 Hz, 6 H), 2.34–2.43 (m, 5 H), 0.97 (t, *J* = 7.6 Hz, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ (*E*/*Z*-mixture) = 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.

Dimethyl (2-Methyl-1-(2-tosylhydrazono)propyl)phosphonate (7c)[21]

Following the general procedure above, the crude residue was purified by recrystallization; yield: 5.15 g (74%); white solid; R_f = 0.30 (EtOAc–PE, 3:1). The *E*/*Z*-isomers were difficult to separate.

^{1}H NMR (400 MHz, DMSO-d_6): δ (*E*/*Z*-mixture) = 11.48 (s, 1 H), 7.73 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 3.50 (d, *J* = 11.2 Hz, 6 H), 3.00–3.14 (m, 1 H), 2.38 (s, 3 H), 1.05 (d, *J* = 6.8 Hz, 3 H).

Dimethyl (4-Phenylbuta-2,3-dien-2-yl)phosphonate (8a)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel; yield: 37 mg (78%); colorless oil; R_f = 0.50 (EtOAc–PE, 1:1).

IR (film): 2953, 1943, 1460, 1256, 1024, 831, 780 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13–7.25 (m, 5 H), 6.29 (qd, *J* = 13.2, 2.8 Hz, 1 H), 3.68 (d, *J* = 11.2 Hz, 3 H), 3.66 (d, *J* = 11.6 Hz, 3 H), 1.81 (dd, *J* = 14.0, 3.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.75 (d, *J* = 2.8 Hz), 132.13 (d, *J* = 8.2 Hz), 128.64 (d, *J* = 1.3 Hz), 127.51 (d, *J* = 1.4 Hz), 126.94 (d, *J* = 2.5 Hz), 95.34 (d, *J* = 16.2 Hz), 92.15 (d, *J* = 187.6 Hz), 52.98 (d, *J* = 5.4 Hz), 52.92 (d, *J* = 6.0 Hz), 14.90 (d, *J* = 5.7 Hz).

EI-MS: *m*/*z* (%) = 238 (M^+, 28), 223 (7), 205 (5), 191 (2), 145 (2), 128 (100), 109 (7), 102 (10), 93 (5), 77 (9).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{12}H_{16}O_3P$: 239.0832; found: 239.0832.

Dimethyl (1-Phenylpenta-1,2-dien-3-yl)phosphonate (8b)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel (EtOAc–PE, 1:1); yield: 42 mg (83%); colorless oil; R_f = 0.5.

IR (film): 2952, 1938, 1458, 1250, 1025, 829, 775 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14–7.27 (m, 5 H), 6.39 (td, *J* = 13.2, 3.2 Hz, 1 H), 3.69 (d, *J* = 11.2 Hz, 3 H), 3.66 (d, *J* = 11.6 Hz, 3 H), 2.20–2.35 (m, 2 H), 1.81 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.13 (d, *J* = 4.9 Hz), 132.43 (d, *J* = 8.4 Hz), 128.77 (d, *J* = 1.3 Hz), 127.62 (d, *J* = 1.9 Hz), 126.87 (d, *J* = 2.6 Hz), 99.21 (d, *J* = 185.7 Hz), 97.30 (d, *J* = 16.3 Hz), 53.09 (d, *J* = 5.7 Hz), 53.03 (d, *J* = 5.9 Hz), 22.31 (d, *J* = 6.4 Hz), 12.57 (d, *J* = 7.8 Hz).

EI-MS: *m*/*z* (%) = 252 (M^+, 30), 237 (30), 219 (5), 205 (11), 175 (5), 142 (100), 128 (79), 115 (60), 102 (11), 93 (10), 77 (9).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{13}H_{18}O_3P$: 253.0988; found: 253.0988.

Dimethyl (4-Methyl-1-phenylpenta-1,2-dien-3-yl)phosphonate (8c)

Following the general procedure described above, the crude residue was purified by column chromatography on silica gel (EtOAc–PE, 1:1); yield: 31 mg (58%); colorless oil; R_f = 0.55.

IR (film): 2963, 1935, 1458, 1250, 1028, 830, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.27 (m, 5 H), 6.40 (dd, *J* = 13.2, 2.0 Hz, 1 H), 3.68 (d, *J* = 10.8 Hz, 3 H), 3.65 (d, *J* = 11.2 Hz, 3 H), 2.55–2.65 (m, 1 H), 1.14 (d, *J* = 6.8 Hz, 3 H), 1.11 (d, *J* = 6.8 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.69 (d, *J* = 4.8 Hz), 132.44 (d, *J* = 8.4 Hz), 128.82 (d, *J* = 1.3 Hz), 127.63 (d, *J* = 1.4 Hz), 136.77 (d, *J* = 2.5 Hz), 104.30 (d, *J* = 183.6 Hz), 97.80 (d, *J* = 16.3 Hz), 53.06 (d, *J* = 6.2 Hz), 53.00 (d, *J* = 6.4 Hz), 29.39 (d, *J* = 6.9 Hz), 22.89 (d, *J* = 5.8 Hz), 22.50 (d, *J* = 5.3 Hz).

EI-MS: *m*/*z* (%) = 266 (M^+, 92), 251 (75), 224 (91), 209 (15), 189 (14), 156 (95), 141 (89), 128 (53), 115 (100), 102 (15), 91 (17), 79 (16).

HRMS (ESI): *m*/*z* [(M + H)$^+$] calcd for $C_{14}H_{20}O_3P$: 267.1145; found: 267.1144.

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Supporting Information

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