Knoevenagel Reaction of Diethylphosphonoacetic Acid: A Facile Route to Diethyl (*E*)-2-Arylvinylphosphonates

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Abstract: Knoevenagel reaction of aromatic aldehydes or α-substituted aliphatic aldehydes with diethylphosphonoacetic acid leads to the formation of 3-substituted-2-(diethoxyphosphoryl)acrylic acids. Decarboxylation of the resulting (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids afforded diethyl (*E*)-2-arylvinylphosphonates. Direct synthesis of diethyl vinylphosphonates from some aromatic aldehydes and formaldehyde is also reported.

Key words, Knoevenagel reaction, vinylphosphonates, decarboxylation, acrylic acids, diethylphosphonoacetic acid

Sequential Knoevenagel condensation of acetic acids bearing different electron-withdrawing groups at C-2 with carbonyl compounds and decarboxylation of the resulting 2-alkenoic acids is a versatile and generally used synthetic approach to the corresponding functionalized olefins. Within this area, the use of malonic acid, malonic monoesters and cyanoacetic acid for carboxyolefination of aldehydes and ketones leading to 2-alkenoic acids, 2-alkenoates and related cyanides, respectively, is well documented.[1] Surprisingly, phosphonoolefination of carbonyl compounds with dialkylphosphonoacetic acids to give α,β-unsaturated phosphonates remains unexplored.

For the past several years there has been considerable interest in the stereoselective synthesis of diethyl 1-alkenylphosphonates due to their use as versatile intermediates both in the synthesis of highly functionalized organophosphorus and organic compounds.[2] A number of synthetic approaches have been reported for this class of phosphonates. They are readily available by Horner–Wadsworth–Emmons reaction of aldehydes with tetraethyl methylenebisphosphonate,[3] palladium-catalyzed reaction of 1-alkenyl bromides with diethyl phosphite,[4] dehydration of β-hydroxyphosphonates[5] and Peterson reaction of aldehydes with diethyl trimethylsilylmethylphosphonate.[6] Other, equally attractive methods involve Heck coupling of aryl bromides, aryldiazonium salts or arylboronic acids with diethyl vinylphosphonate,[7] cross metathesis of diethyl vinylphosphonate with terminal olefins,[8] reduction of the corresponding 1-alkynylphosphonates[9] and finally palladium-catalyzed reaction of *E*- and *Z*-alkenylboronic acids with triethylphosphite.[10] Although these protocols have found widespread utility there is still a great need for cheaper methods using more accessible starting materials.

Recently, we have been exploring the condensations of diethylphosphonoacetic acid (**1**) with formaldehyde as an effective route to 1-(aminomethyl)vinylphosphonates,[11] 1-(alkoxymethyl)vinylphosphonates[12] and dicyclohexylammonium 2-(diethoxyphosphoryl)acrylate.[13] Among others, we have found that a mixture of β-alanine and AcOH is a versatile catalyst for the Knoevenagel reaction of the acid **1** with isobutyraldehyde (**2j**) producing (*E*,*Z*)-2-diethoxyphosphoryl-4-methyl-2-pentenoic acid (**3j**).[12]

In this paper we demonstrate that such a type of condensation has general applicability and can be treated as a convenient source of differently substituted 2-(diethoxyphosphoryl)acrylic acids **3**. Moreover, we show that the novel condensation together with subsequent decarboxylation of the acids **3** constitutes particularly advantageous and atom economic approach to (*E*)-2-arylvinylphosphonates. Additionally, direct phosphonoolefination of some aromatic aldehydes and formaldehyde with the acid **1** is described.

We began our investigations with the goal of finding the most suitable conditions for the preparation of acrylic acids **3**. Various aliphatic and aromatic aldehydes were reacted with the acid **1** in boiling benzene in the presence of β-alanine (10 mol%) and AcOH (27 mol%) with azeotropic removal of water (Scheme 1).

In order to achieve high conversion of the acid **1** in a short period of time 1.3 equivalents of aldehyde were routinely used. The amounts of β-alanine and AcOH were held constant. The progress of each reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. The reactions with several aldehydes **2a**–**k** were terminated within 20 to 22 hours providing the alkenoic acids **3a**–**k**, each as a mixture of *E* and *Z* isomers with close to a 6:1 ratio. Data collected in Table 1 show that catalytic system proved to be versatile with respect not only to the condensation of α-substituted aldehydes **2j**,**k** but also aromatic aldehydes **2a**–**i** containing electron-withdrawing or electron-donating substituents on the aromatic ring. No reaction was observed with α-unsubstituted aliphatic aldehydes, *m*- and *p*-hydroxybenzaldehydes or indole-3-carboxaldehyde.

The crude (*E*,*Z*)-alkenoic acids **3a**–**k** were then converted into the dicyclohexylammonium salts **4a**–**k**. Conveniently, the crystalline salts **4a**–**k** were isolated as the *E* isomers, exclusively. We believe that *Z* to *E* isomerization of

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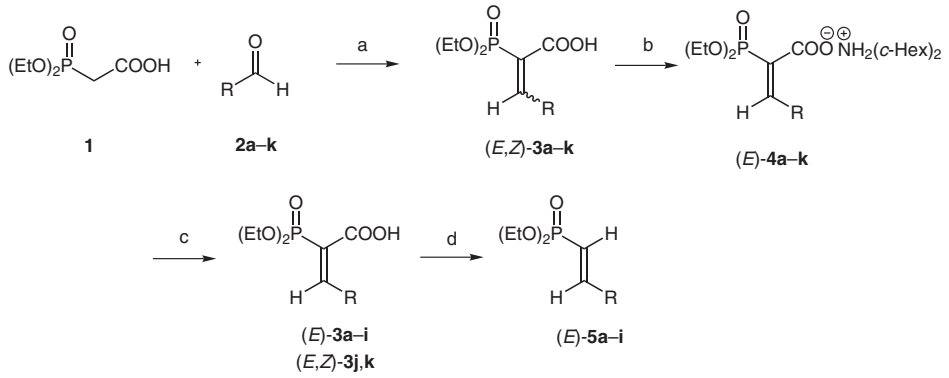


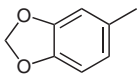
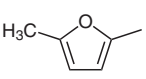
Scheme 1 *Reagents and conditions:* (a) 27 mol% CH_3COOH, 10 mol% β-alanine, benzene, reflux, 20–22 h.; (b) $(c\text{-Hex})_2NH$, benzene, r.t.; (c) ion-exchange chromatography; (d) 40 mol% piperidine, toluene, reflux, 2 h.

the acids **3a**–**k** is induced by thermodynamically controlled Michael addition and readdition of dicyclohexylamine. The salts (*E*)-**4a**–**i** were converted into the corresponding *E*-acrylic acids **3a**–**i** by ion-exchange chromatography in nearly quantitative yields. The ion-exchange chromatography of the alkenoates **4j**,**k** was accompanied by their partial isomerization. The corresponding acids **3j**,**k** were isolated as mixtures of *E* and *Z* isomers in ratios 6:1 and 95:5, respectively.

With the suitable substrates in hand, we turned our attention to their effective conversion into vinylphosphonates **5**. Guided by the knowledge of pyridine-catalyzed decarboxylation of arylidenemalonic acids,[14] we have devised a method for the decarboxylation of the acrylic acids **3a**–**k** using piperidine as a catalyst (Scheme 1, Table 1). The acids **3a**–**k** were heated in boiling toluene in the presence of a catalytic amount of piperidine (40 mol%) for two hours. Under these conditions the decarboxylation of (*E*)-3-arylacrylic acids **3a**–**i** proved to be highly efficient providing the corresponding (*E*)-2-arylvinylphosphonates **5a**–**i** in fully stereoselective manner. None of the *Z* isomers were detected by NMR analysis of the crude reaction mixture. However, this method proved to be ineffective for decarboxylation of the alkenoic acids **3j**,**k**. The resulting (*E*)-2-arylvinylphosphonates **5a**–**i** were purified by column chromatography and their physical properties were found to be identical with those given in the literature. The structures of new compounds were assigned on the basis of the corresponding spectral data.

It occurred to us that the formation of the acids **3** and their decarboxylation could be carried out in a single synthetic operation by a proper choice of the solvent and catalyst.

Table 1 Dicyclohexylammonium Acrylates **4a**–**k**, Phosphonoacrylic Acids **3a**–**k** and Vinylphosphonates **5a**–**i** Prepared

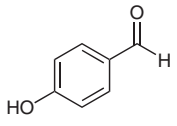
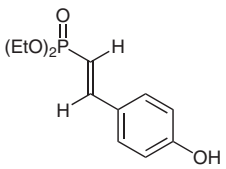
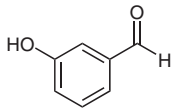
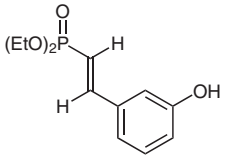
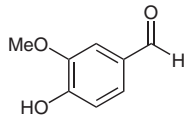
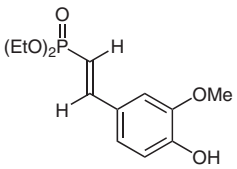
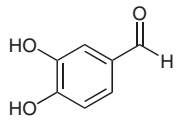
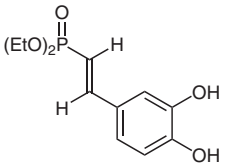
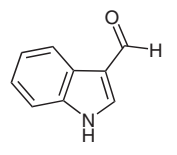
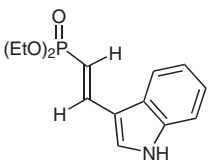
Entry	R	Yield (%)		
		Dicyclohexylammonium acrylate **4**	Acrylic acid **3**	Vinylphosphonate **5**
a	4-$NO_2C_6H_4$	82	96	89
b	3-$NO_2C_6H_4$	74	91	83
c	4-$CH_3C_6H_4$	76	95	80
d	4-$CH_3OC_6H_4$	73	93	84
e	3,4-$(CH_3O)_2C_6H_3$	71	92	81
f		75	94	81
g	4-BrC_6H_4	77	94	82
h		67	89	86
i		70	91	77
j	$(CH_3)_2CH$	69	95	–
k	cC_6H_{11}	71	94	–

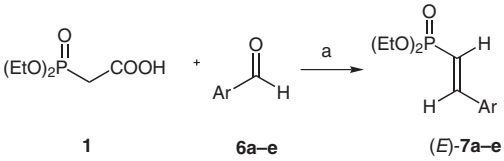
To validate this hypothesis piperidine–AcOH was examined as the catalyst of the selected condensations. The reaction of aldehydes **2a–k** with the acid **1** performed in boiling benzene in the presence of a catalytic amount of piperidine (27 mol%) and AcOH (20 mol%) failed to give any products. However, changing the solvent to toluene brought some interesting results.

The reactions of the acid **1** with aliphatic aldehydes **2j**,**k** performed in boiling toluene were not chemoselective. Under the same conditions aromatic aldehydes **2a–i** afforded the corresponding vinylphosphonates **5a–i** accompanied by small amounts of other organophosphorus compounds and unreacted starting material. In practice, the one-pot methodology could be effectively applied to benzaldehydes **6a–d** bearing hydroxy group on the aromatic ring and indole 3-carboxaldehyde (**6e**) (Scheme 2, Table 2). All these reactions were terminated within 20 hours and the resulting *E*-vinylphosphonates **7a–e** were isolated by column chromatography.

In parallel investigations, we studied the condensation of formaldehyde with the acid **1** as a route to diethyl vinylphosphonate (**9**). In one of our previous papers we reported on the synthesis of dicyclohexylammonium 2-(diethoxyphosphoryl)acrylate (**8**).[13] We found that this

Table 2 Vinylphosphonates **7a–e** Prepared

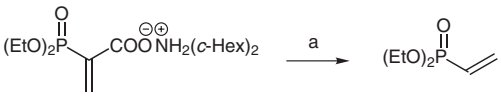
Entry	Aldehyde **6**	Vinylphosphonate **7**	Yield (%)
a			82
b			68
c			80
d			79
e			76



1 **6a–e** (*E*)-**7a–e**

Scheme 2 *Reagents and conditions:* (a) 20 mol% CH_3COOH, 27 mol% piperidine, toluene, reflux, 20 h.

compound was thermally unstable and underwent decomposition to give the phosphonate **9** on heating in boiling benzene. Our recent efforts to optimize the synthesis of the phosphonate **9** have led to remarkable observation that efficiency of the decarboxylation can be improved significantly by using DABCO as a catalyst (Scheme 3).



8 **9**

Scheme 3 *Reagents and conditions:* (a) 1 equiv DABCO, benzene, reflux.

It is likely that the above reaction involves addition of DABCO to the acrylic acid **10** to give the zwitterionic intermediate **11** followed by spontaneous decarboxylative elimination of the latter in tautomeric form of the carboxylate anion **12** (Scheme 4).

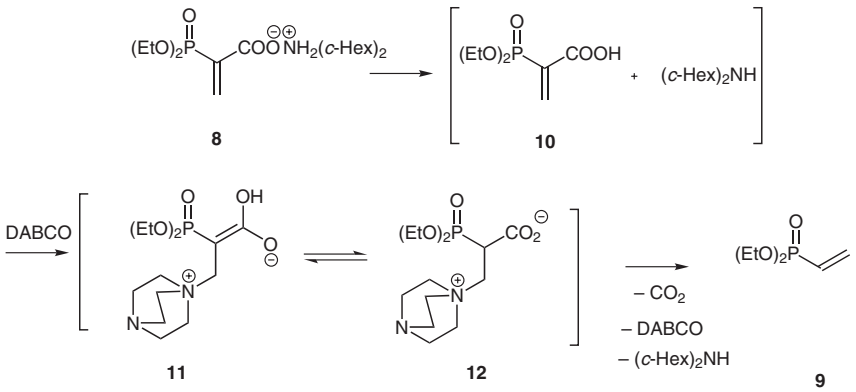
Based on these results we have come to the conclusion that the vinylphosphonate **9** can be obtained directly from formaldehyde and the acid **1**. Indeed, the reaction of the acid **1** with excess of formaldehyde performed in boiling benzene in the presence of catalytic amounts of dicyclohexylamine (15 mol%) and DABCO (15 mol%) afforded the phosphonate **9** in 73% yield (Scheme 5).

In summary, we have developed a novel and effective method for the synthesis of diethyl vinylphosphonates based on the Knoevenagel type reaction of aromatic aldehydes and formaldehyde with diethylphosphonoacetic acid. Particular attention has been paid to the generality of the process that guarantees the synthesis of a range of (*E*)-2-arylvinylphosphonates in good yields and in a stereoselective manner.

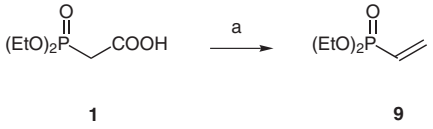
NMR spectra were recorded on a Bruker DPX 250 instrument at 250.13 MHz for ^{1}H, 62.9 MHz for ^{13}C and 101.3 MHz for ^{31}P NMR, using TMS as internal and 85% H_3PO_4 as external standard. The multiplicity of carbons was determined by DEPT experiments. IR spectra were measured on a Specord M80 (Zeiss) instrument. Elemental analyses were performed on a Perkin–Elmer PE 2400 analyzer. Melting points were determined in open capillaries and are uncorrected. Diethylphosphonoacetic acid (**1**) was prepared according to the literature procedure.[15]

Dicyclohexylammonium (*E*)-2-(Diethoxyphosphoryl)acrylates (4); General Procedure

A mixture of diethylphosphonoacetic acid (**1**; 19.6 g, 0.1 mol), aldehyde **2** (0.13 mol), β-alanine (0.89 g, 0.01 mol) and AcOH (1.62



Scheme 4



Scheme 5 *Reagents and conditions:* (a) 2.2 equiv $(HCHO)_n$, 15 mol% DABCO, 15 mol% $(c\text{-Hex})_2NH$, benzene, reflux.

g, 0.027 mol) in benzene (200 mL) was heated at reflux under Dean–Stark water separator for 20–22 h. The reaction progress was occasionally monitored with ^{31}P NMR. After the acid **1** was completely consumed, dicyclohexylamine was added (18.1 g, 0.1 mol) and the solvent was evaporated. The solid residue was suspended in Et_2O and the crystals were collected by filtration to afford the crude product. Recrystallization of the solid from CH_2Cl_2–acetone afforded the acrylate **4**.

Dicyclohexylammonium (*E*)-2-Diethoxyphosphoryl-3-(4-nitrophenyl)acrylate (4a)
Yield: 82%; pale yellow crystals; mp 155–157 °C.

IR (CCl_4): 2936, 1628, 1528, 1348, 1240, 1108, 1024, 968, 784 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.99–1.27 (m, 6 H, 3 × CH_2), 1.37 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × C*H*$_3$CH$_2$OP), 1.38–1.51 (m, 4 H, 2 × CH_2), 1.62–1.77 (m, 6 H, 3 × CH_2), 1.95–1.99 (m, 4 H, 2 × CH_2), 2.88–2.98 (m, 2 H, 2 × CHN), 4.15–4.26 (m, 4 H, 2 × CH_3C*H*$_2$OP), 7.15 (d, $^3J_{HP}$ = 25.8 Hz, 1 H, CHAr), 7.85 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}), 8.14 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 16.79.

Anal. Calcd for $C_{25}H_{39}N_2O_7P$: C, 58.81; H, 7.70. Found: C, 58.94; H, 7.76.

Dicyclohexylammonium (*E*)-2-Diethoxyphosphoryl-3-(3-nitrophenyl)acrylate (4b)
Yield: 74%; white crystals; mp 124–126 °C.

IR (CCl_4): 2936, 1628, 1532, 1352, 1248, 1032, 964, 760 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.90–1.29 (m, 6 H, 3 × CH_2), 1.37 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × C*H*$_3$CH$_2$OP), 1.40–1.62 (m, 6 H, 3 × CH_2), 1.71–1.76 (m, 4 H, 2 × CH_2), 1.97–2.01 (m, 4 H, 2 × CH_2), 2.89–2.98 (m, 2 H, 2 × CHN), 4.16–4.26 (m, 4 H, 2 × CH_3C*H*$_2$OP), 7.15 (d, $^3J_{HP}$ = 26.0 Hz, 1 H, CHAr), 7.48 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 7.95 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 8.14 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 8.66 (s, 1 H, CH_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 17.27.

Anal. Calcd for $C_{25}H_{39}N_2O_7P$: C, 58.81; H, 7.70. Found: C, 58.94; H, 7.78.

Dicyclohexylammonium (*E*)-2-Diethoxyphosphoryl-3-(*p*-tolyl)acrylate (4c)
Yield: 76%; white crystals; mp 157–159 °C.

IR (CCl_4): 2984, 1628, 1392, 1264, 1028, 952, 764 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.03–1.24 (m, 6 H, 3 × CH_2), 1.34 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, 2 × C*H*$_3$CH$_2$OP), 1.41–1.61 (m, 6 H, 3 × CH_2), 1.70–1.74 (m, 4 H, 2 × CH_2), 1.94–1.99 (m, 4 H, 2 × CH_2), 2.32 (s, 3 H, CH_3Ar), 2.85–2.94 (m, 2 H, 2 × CHN), 4.13–4.25 (m, 4 H, 2 × CH_3C*H*$_2$OP), 7.08 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 2 × CH_{Ar}), 7.11 (d, $^3J_{HP}$ = 26.5 Hz, 1 H, CHAr), 7.59 (d, $^3J_{HH}$ = 8.1 Hz, 2 H, 2 × CH_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 19.06.

Anal. Calcd for $C_{26}H_{42}NO_5P$: C, 65.11; H, 8.83. Found: C, 65.00; H, 8.76.

Dicyclohexylammonium (*E*)-2-Diethoxyphosphoryl-3-(4-methoxyphenyl)acrylate (4d)
Yield: 73%; white crystals; mp 160–162 °C.

IR (CCl_4): 2936, 1628, 1512, 1396, 1240, 1176, 1024, 756 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 0.96–1.26 (m, 6 H, 3 × CH_2), 1.34 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, 2 × C*H*$_3$CH$_2$OP), 1.41–1.61 (m, 6 H, 3 × CH_2), 1.70–1.75 (m, 4 H, 2 × CH_2), 1.95–2.00 (m, 4 H, 2 × CH_2), 2.88–2.97 (m, 2 H, 2 × CHN), 3.80 (s, 3 H, CH_3OAr), 4.12–4.24 (m, 4 H, 2 × CH_3C*H*$_2$OP), 6.80 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}), 7.08 (d, $^3J_{HP}$ = 26.5 Hz, 1 H, CHAr), 7.67 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 19.45.

Anal. Calcd for $C_{26}H_{42}NO_6P$: C, 63.01; H, 8.54. Found: C, 62.88; H, 8.47.

Dicyclohexylammonium (*E*)-2-Diethoxyphosphoryl-3-(3,4-dimethoxyphenyl)acrylate (4e)
Yield: 71%; white crystals; mp 155–157 °C.

IR (CCl_4): 2936, 1628, 1600, 1508, 1396, 1320, 1236, 1132, 1020, 952, 784 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.03–1.24 (m, 6 H, 3 × CH_2), 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, 2 × C*H*$_3$CH$_2$OP), 1.43–1.61 (m, 6 H, 3 × CH_2), 1.69–1.74 (m, 4 H, 2 × CH_2), 1.94–1.98 (m, 4 H, 2 × CH_2), 2.83–2.92 (m, 2 H, 2 × CHN), 3.85 (s, 3 H, CH_3OAr), 3.86 (s, 3 H, CH_3OAr), 4.13–4.24 (m, 4 H, 2 × CH_3C*H*$_2$OP), 6.76 (d, $^3J_{HH}$ = 9.0 Hz, 1 H, CH_{Ar}), 7.07 (d, $^3J_{HP}$ = 26.5 Hz, 1 H, CHAr), 7.30 (d, $^3J_{HH}$ = 9.0 Hz, 1 H, CH_{Ar}), 7.32 (s, 1 H, CH_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 19.43.

Anal. Calcd for $C_{27}H_{44}NO_7P$: C, 61.70; H, 8.44. Found: C, 61.59; H, 8.35.

Dicyclohexylammonium (*E*)-3-Benzo[1,3]dioxol-5-yl-2-(diethoxyphosphoryl)acrylate (4f)
Yield: 75%; white crystals; mp 157–159 °C.

IR (CCl_4): 2936, 1624, 1548, 1488, 1440, 1400, 1304, 1240, 1200, 1100, 1020, 968, 784 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.05–1.24 (m, 6 H, 3 × CH_2), 1.34 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 1.42–1.60 (m, 6 H, 3 × CH_2), 1.71–1.76 (m, 4 H, 2 × CH_2), 1.97–2.01 (m, 4 H, 2 × CH_2), 2.90–2.99 (m, 2 H, 2 × CHN), 4.11–4.25 (m, 4 H, 2 × CH$_3$CH_2OP), 5.93 (s, 2 H, CH_2O_2Ar), 6.73 (d, $^3J_{HH}$ = 8.3 Hz, 1 H, CH_{Ar}), 7.03 (d, $^3J_{HP}$ = 26.3 Hz, 1 H, CHAr), 7.10 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, CH_{Ar}), 7.42 (d, $^4J_{HH}$ = 1.5 Hz, 1 H, CH_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 19.22.

Anal. Calcd for $C_{26}H_{40}NO_7P$: C, 61.28; H, 7.91. Found: C, 61.13; H, 7.84.

Dicyclohexylammonium (*E*)-2-Diethoxyphosphoryl-3-(4-bromophenyl)acrylate (4g)
Yield: 77%; white crystals; mp 156–158 °C.

IR (CCl_4): 2936, 1624, 1520, 1464, 1384, 1312, 1248, 1100, 1028, 784 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.01–1.27 (m, 6 H, 3 × CH_2), 1.35 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 1.43–1.65 (m, 6 H, 3 × CH_2), 1.73–1.78 (m, 4 H, 2 × CH_2), 1.95–2.00 (m, 4 H, 2 × CH_2), 2.87–2.97 (m, 2 H, 2 × CHN), 4.09–4.25 (m, 4 H, 2 × CH$_3$CH_2OP), 7.07 (d, $^3J_{HP}$ = 26.0 Hz, 1 H, CHAr), 7.40 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2 × CH_{Ar}), 7.56 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2 × CH_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 17.95.

Anal. Calcd for $C_{25}H_{39}BrNO_5P$: C, 55.15; H, 7.22. Found: C, 55.29; H, 7.31.

Dicyclohexylammonium (*E*)-2-(Diethoxyphosphoryl)-3-(furan-2-yl)acrylate (4h)
Yield: 67%; pale yellow crystals; mp 141–143 °C.

IR (CCl_4): 2936, 1628, 1556, 1384, 1296, 1236, 1160, 1020, 784 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.07–1.24 (m, 6 H, 3 × CH_2), 1.34 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, 2 × CH_3CH$_2$OP), 1.46–1.62 (m, 6 H, 3 × CH_2), 1.72–1.77 (m, 4 H, 2 × CH_2), 2.03–2.07 (m, 4 H, 2 × CH_2), 2.95–3.04 (m, 2 H, 2 × CHN), 4.12–4.23 (m, 4 H, 2 × CH$_3$CH_2OP), 6.40 (dd, $^3J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, CH_{Ar}), 6.89 (d, $^3J_{HH}$ = 3.4 Hz, 1 H, CH_{Ar}), 6.99 (d, $^3J_{HP}$ = 25.8 Hz, 1 H, CHAr), 7.38 (d, $^3J_{HH}$ = 1.8 Hz, 1 H, CH_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 18.61.

Anal. Calcd for $C_{23}H_{38}NO_6P$: C, 60.64; H, 8.41. Found: C, 60.51; H, 8.34.

Dicyclohexylammonium (*E*)-2-(Diethoxyphosphoryl)-3-(5-methylfuran-2-yl)acrylate (4i)
Yield: 70%; yellow crystals; mp 141–143 °C.

IR (CCl_4): 2936, 1624, 1392, 1248, 1032, 964, 800 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.05–1.23 (m, 6 H, 3 × CH_2), 1.33 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 1.45–1.61 (m, 6 H, 3 × CH_2), 1.71–1.76 (m, 4 H, 2 × CH_2), 2.01–2.06 (m, 4 H, 2 × CH_2), 2.28 (s, 3 H, CH_3Ar), 2.94–3.03 (m, 2 H, 2 × CHN), 4.11–4.22 (m, 4 H, 2 × CH$_3$CH_2OP), 6.00 (d, $^3J_{HH}$ = 2.8 Hz, 1 H, CH_{Ar}), 6.86 (d, $^3J_{HH}$ = 2.8 Hz, 1 H, CH_{Ar}), 6.96 (d, $^3J_{HP}$ = 25.8 Hz, 1 H, CHAr).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 19.26.

Anal. Calcd for $C_{24}H_{40}NO_6P$: C, 61.39; H, 8.59. Found: C, 61.29; H, 8.50.

Dicyclohexylammonium (*E*)-2-(Diethoxyphosphoryl)-4-methyl-2-pentenoate (4j)
Yield: 69%; white crystals; mp 106–108 °C.

IR (CCl_4): 2936, 1624, 1392, 1328, 1280, 1244, 1160, 1036, 792 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.05 [d, $^3J_{HH}$ = 6.5 Hz, 6 H, (CH_3)$_2$CH], 1.13–1.30 (m, 6 H, 3 × CH_2), 1.31 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 1.46–1.65 (m, 6 H, 3 × CH_2), 1.76–1.79 (m, 4 H, 2 × CH_2), 2.01–2.06 (m, 4 H, 2 × CH_2), 2.93–3.05 (m, 2 H, 2 × CHN), 3.02–3.16 [m, 1 H, (CH$_3$)$_2$CH], 4.06–4.18 (m, 4 H, 2 × CH$_3$CH_2OP), 6.29 (dd, $^3J_{HP}$ = 24.2 Hz, $^3J_{HH}$ = 9.5 Hz, 1 H, C=CH).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 18.96.

Anal. Calcd for $C_{22}H_{42}NO_5P$: C, 61.23; H, 9.81. Found: C, 61.35; H, 9.92.

Dicyclohexylammonium (*E*)-3-Cyclohexyl-2-(diethoxyphosphoryl)acrylate (4k)
Yield: 71%; white crystals; mp 132–134 °C.

IR (CCl_4): 2936, 1624, 1448, 1396, 1316, 1244, 1164, 1032, 960, 776 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.06–1.22 (m, 11 H, CH_2), 1.31 (dt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 × CH_3CH$_2$OP), 1.47–1.81 (m, 15 H, CH_2), 2.02–2.06 (m, 4 H, CH_2), 2.81–2.84 [m, 1 H, (CH$_2$)$_5$CH], 2.92–3.02 (m, 2 H, 2 × CHN), 4.06–4.17 (m, 4 H, 2 × CH$_3$CH_2OP), 6.32 (dd, $^3J_{HP}$ = 24.5 Hz, $^3J_{HH}$ = 9.5 Hz, 1 H, C=CH).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 19.38.

Anal. Calcd for $C_{25}H_{46}NO_5P$: C, 63.67; H, 9.83. Found: C, 63.75; H, 9.91.

2-(Diethoxyphosphoryl)acrylic Acids (3); General Procedure
Ion-exchange chromatography of the salts **4a–k** (0.05 mol) was performed on a glass column packed with Dowex 50W using H_2O–acetone (1:1) as eluent. The eluent was evaporated to give an oily residue. The residue was dissolved in acetone and after evaporation of the solvent it was left to crystallize. The solid was suspended in Et_2O, collected by filtration and air-dried.

(*E*)-2-Diethoxyphosphoryl-3-(4-nitrophenyl)acrylic Acid (3a)
Yield: 96%; pale yellow crystals; mp 147–149 °C.

IR (CCl_4): 2864, 1708, 1592, 1520, 1376, 1192, 1032, 760 cm^{-1}.

^1H NMR (250 MHz, acetone-d_6): δ = 1.34 (dt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 × CH_3CH$_2$OP), 4.12–4.24 (m, 4 H, 2 × CH$_3$CH_2OP), 7.65 (d, $^3J_{HP}$ = 24.0 Hz, 1 H, CHAr), 7.85 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}), 8.30 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 16.38 (d, $^3J_{CP}$ = 6.2 Hz, 2 × CH_3CH$_2$OP), 63.66 (d, $^2J_{CP}$ = 5.0 Hz, 2 × CH$_3$CH$_2$OP), 124.38 (2 × CH_{Ar}), 130.82 (2 × CH_{Ar}), 130.82 (d, $^1J_{CP}$ = 175.0 Hz, PC), 141.12 (d, $^3J_{CP}$ = 21.0 Hz, C_{Ar}), 144.21 (d, $^2J_{CP}$ = 6.1 Hz, CHAr), 149.06 (C_{Ar}), 167.16 (d, $^2J_{CP}$ = 11.5 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 12.19.

Anal. Calcd for $C_{13}H_{16}NO_7P$: C, 47.42; H, 4.90. Found: C, 47.24; H, 4.77.

(*E*)-2-Diethoxyphosphoryl-3-(3-nitrophenyl)acrylic Acid (3b)
Yield: 91%; white crystals; mp 118–120 °C.

IR (CCl_4): 2984, 2528, 1708, 1624, 1528, 1352, 1200, 1012, 784 cm^{-1}.

^1H NMR (250 MHz, acetone-d_6): δ = 1.34 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 4.12–4.24 (m, 4 H, 2 × CH$_3$CH_2OP), 7.65 (d,

$^3J_{HP}$ = 24.0 Hz, 1 H, CHAr), 7.77 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 8.02 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 8.30 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 8.50 (s, 1 H, CH_{Ar}).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 16.47 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH_3CH_2OP), 63.77 (d, $^2J_{CP}$ = 5.2 Hz, 2 × CH_3CH_2OP), 124.21 (CH_{Ar}), 125.25 (CH_{Ar}), 129.56 (d, $^1J_{CP}$ = 174.9 Hz, PC), 130.95 (CH_{Ar}), 136.00 (CH_{Ar}), 136.50 (d, $^3J_{CP}$ = 21.4 Hz, C_{Ar}), 144.73 (d, $^2J_{CP}$ = 6.5 Hz, CHAr), 149.18 (C_{Ar}), 167.18 (d, $^2J_{CP}$ = 11.8 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 12.30.

Anal. Calcd for $C_{13}H_{16}NO_7P$: C, 47.42; H, 4.90. Found: C, 47.28; H, 4.78.

(*E*)-2-Diethoxyphosphoryl-3-(*p*-tolyl)acrylic Acid (3c)
Yield: 95%; white crystals; mp 96–98 °C.

IR (CCl_4): 2912, 1708, 1608, 1512, 1400, 1300, 1288, 1184, 1040, 964, 792 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 1.32 (dt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 0.3 Hz, 6 H, 2 × CH_3CH$_2$OP), 2.36 (s, 3 H, CH_3Ar), 4.08–4.19 (m, 4 H, 2 × CH_3CH_2OP), 7.25 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2 × CH_{Ar}), 7.47 (d, $^3J_{HP}$ = 24.5 Hz, 1 H, CHAr), 7.51 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2 × CH_{Ar}).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 16.47 (d, $^3J_{CP}$ = 6.5 Hz, 2 × CH_3CH_2OP), 31.34 (CH_3Ar), 63.38 (d, $^2J_{CP}$ = 5.1 Hz, 2 × CH_3CH_2OP), 124.93 (d, $^1J_{CP}$ = 178.3 Hz, PC), 130.18 (2 × CH_{Ar}), 130.25 (2 × CH_{Ar}), 131.94 (d, $^3J_{CP}$ = 20.8 Hz, C_{Ar}), 141.67 (C_{Ar}), 147.03 (d, $^2J_{CP}$ = 6.2 Hz, CHAr), 167.91 (d, $^2J_{CP}$ = 12.5 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 14.13.

Anal. Calcd for $C_{14}H_{19}O_5P$: C, 56.37; H, 6.42. Found: C, 56.27; H, 6.35.

(*E*)-2-Diethoxyphosphoryl-3-(4-methoxyphenyl)acrylic Acid (3d)
Yield: 93%; white crystals; mp 95–97 °C.

IR (CCl_4): 2912, 1708, 1608, 1512, 1308, 1192, 1012, 788 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 1.31 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 3.85 (s, 3 H, CH_3OAr), 4.07–4.18 (m, 4 H, 2 × CH_3CH_2OP), 6.99 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}), 7.45 (d, $^3J_{HP}$ = 24.6 Hz, 1 H, CHAr), 7.61 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 16.44 (d, $^3J_{CP}$ = 6.7 Hz, 2 × CH_3CH_2OP), 55.72 (CH_3OAr), 63.25 (d, $^2J_{CP}$ = 5.2 Hz, 2 × CH_3CH_2OP), 114.90 (2 × CH_{Ar}), 122.63 (d, $^1J_{CP}$ = 179.83 Hz, PC), 127.01 (d, $^3J_{CP}$ = 21.2 Hz, C_{Ar}), 132.32 (2 × CH_{Ar}), 147.00 (d, $^2J_{CP}$ = 6.5 Hz, CHAr), 162.43 (C_{Ar}), 168.08 (d, $^2J_{CP}$ = 12.6 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 14.73.

Anal. Calcd for $C_{14}H_{19}O_6P$: C, 53.50; H, 6.09. Found: C, 53.38; H, 6.01.

(*E*)-2-Diethoxyphosphoryl-3-(3,4-dimethoxyphenyl)acrylic Acid (3e)
Yield: 92%; white crystals; mp 126–128 °C.

IR (CCl_4): 2936, 1708, 1596, 1516, 1276, 1024, 976, 784 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 1.31 (dt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 × CH_3CH$_2$OP), 3.81 (s, 3 H, CH_3OAr), 3.86 (s, 3 H, CH_3OAr), 4.07–4.19 (m, 4 H, 2 × CH_3CH_2OP), 6.99 (d, $^3J_{HH}$ = 8.3 Hz, 1 H, CH_{Ar}), 7.23 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.2 Hz, 1 H, CH_{Ar}), 7.29 (d, $^4J_{HH}$ = 2.2 Hz, 1 H, CH_{Ar}), 7.43 (d, $^3J_{HP}$ = 24.5 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 16.46 (d, $^3J_{CP}$ = 6.5 Hz, 2 × CH_3CH_2OP), 55.99 (CH_3OAr), 56.03 (CH_3OAr), 63.13 (d, $^2J_{CP}$ = 5.1 Hz, 2 × CH_3CH_2OP), 112.22 (CH_{Ar}), 113.35 (CH_{Ar}), 123.14 (d, $^1J_{CP}$ = 181.6 Hz, PC), 124.58 (CH_{Ar}), 127.26 (d, $^3J_{CP}$ = 21.1 Hz, C_{Ar}), 146.91 (d, $^2J_{CP}$ = 6.4 Hz, CHAr), 150.04 (C_{Ar}), 150.44 (C_{Ar}), 168.25 (d, $^2J_{CP}$ = 12.4 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 14.82.

Anal. Calcd for $C_{15}H_{21}O_7P$: C, 52.33; H, 6.15. Found: C, 52.18; H, 6.08.

(*E*)-3-Benzo[1,3]dioxol-5-yl-2-(diethoxyphosphoryl)acrylic Acid (3f)
Yield: 94%; white crystals; mp 149–151 °C.

IR (CCl_4): 2920, 1712, 1600, 1488, 1448, 1260, 1192, 1016, 784 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 1.31 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 × CH_3CH$_2$OP), 4.06–4.18 (m, 4 H, 2 × CH_3CH_2OP), 6.08 (s, 2 H, CH_2O_2Ar), 6.92 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 7.16 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 7.18 (s, 1 H, CH_{Ar}), 7.39 (d, $^3J_{HP}$ = 24.5 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 16.49 (d, $^3J_{CP}$ = 6.5 Hz, 2 × CH_3CH_2OP), 62.99 (d, $^2J_{CP}$ = 5.0 Hz, 2 × CH_3CH_2OP), 102.79 (CH_2O_2Ar), 108.92 (CH_{Ar}), 109.19 (CH_{Ar}), 124.25 (d, $^1J_{CP}$ = 177.0 Hz, PC), 126.61 (CH_{Ar}), 128.88 (d, $^3J_{CP}$ = 21.1 Hz, C_{Ar}), 146.19 (d, $^2J_{CP}$ = 6.3 Hz, CHAr), 149.10 (C_{Ar}), 150.57 (C_{Ar}), 168.04 (d, $^2J_{CP}$ = 12.1 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 14.30.

Anal. Calcd for $C_{14}H_{17}O_7P$: C, 51.23; H, 5.22. Found: C, 51.03; H, 5.14.

(*E*)-2-Diethoxyphosphoryl-3-(4-bromophenyl)acrylic Acid (3g)
Yield: 94%; white crystals; mp 106–108 °C.

IR (CCl_4): 2912, 1712, 1528, 1484, 1396, 1204, 1032, 760 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 1.32 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 × CH_3CH$_2$OP), 4.09–4.21 (m, 4 H, 2 × CH_3CH_2OP), 7.50 (d, $^3J_{HP}$ = 24.0 Hz, 1 H, CHAr), 7.54–7.66 (m, 4 H, 4 × CH_{Ar}).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 16.47 (d, $^3J_{CP}$ = 6.5 Hz, 2 × CH_3CH_2OP), 63.50 (d, $^2J_{CP}$ = 5.2 Hz, 2 × CH_3CH_2OP), 124.93 (C_{Ar}), 127.34 (d, $^1J_{CP}$ = 177.06 Hz, PC), 131.81 (2 × CH_{Ar}), 132.66 (2 × CH_{Ar}), 133.96 (d, $^3J_{CP}$ = 21.0 Hz, C_{Ar}), 145.74 (d, $^2J_{CP}$ = 6.5 Hz, CHAr), 167.45 (d, $^2J_{CP}$ = 12.1 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 14.73.

Anal. Calcd for $C_{13}H_{16}BrO_5P$: C, 43.00; H, 4.44. Found: C, 42.87; H, 4.32.

(*E*)-2-(Diethoxyphosphoryl)-3-(furan-2-yl)acrylic Acid (3h)
Yield: 89%; pale yellow crystals; mp 85–87 °C.

IR (CCl_4): 2864, 2552, 1716, 1620, 1544, 1472, 1392, 1188, 1016, 792 cm^{-1}.

^{1}H NMR (250 MHz, acetone-d_6): δ = 1.32 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.6 Hz, 6 H, 2 × CH_3CH$_2$OP), 4.08–4.19 (m, 4 H, 2 × CH_3CH_2OP), 6.63 (dd, $^3J_{HH}$ = 3.5 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, CH_{Ar}), 7.10 (d, $^3J_{HH}$ = 3.5 Hz, 1 H, CH_{Ar}), 7.34 (d, $^3J_{HP}$ = 24.0 Hz, 1 H, CHAr), 7.75 (d, $^3J_{HH}$ = 1.8 Hz, 1 H, CH_{Ar}).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 16.38 (d, $^3J_{CP}$ = 6.6 Hz, 2 × CH_3CH_2OP), 63.47 (d, $^2J_{CP}$ = 5.2 Hz, 2 × CH_3CH_2OP), 113.45 (CH_{Ar}), 118.57 (CH_{Ar}), 120.28 (d, $^1J_{CP}$ = 182.4 Hz, PC), 133.72 (d, $^2J_{CP}$ = 8.0 Hz, CHAr), 147.05 (CH_{Ar}), 150.28 (d, $^3J_{CP}$ = 24.3 Hz, C_{Ar}), 166.93 (d, $^2J_{CP}$ = 11.8 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 14.67.

Anal. Calcd for $C_{11}H_{15}O_6P$: C, 48.18; H, 5.51. Found: C, 48.01; H, 5.39.

(*E*)-2-(Diethoxyphosphoryl)-3-(5-methylfuran-2-yl)acrylic Acid (3i)
Yield: 91%; yellow crystals; mp 154–156 °C.

IR (CCl_4): 2904, 2544, 1712, 1624, 1588, 1512, 1368, 1348, 1188, 1092, 760 cm^{-1}.

^1H NMR (250 MHz, acetone-d_6): δ = 1.31 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 2.33 (s, 3 H, CH$_3$Ar), 4.06–4.17 (m, 4 H, 2 × CH$_3$CH_2OP), 6.26 (d, $^3J_{HH}$ = 3.2 Hz, 1 H, CH$_{Ar}$), 7.06 (d, $^3J_{HH}$ = 3.2 Hz, 1 H, CH$_{Ar}$), 7.27 (d, $^3J_{HP}$ = 23.8 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, acetone-d_6): δ = 13.71 (CH$_3$Ar), 16.50 (d, $^3J_{CP}$ = 6.5 Hz, 2 × CH$_3$CH$_2$OP), 62.95 (d, $^2J_{CP}$ = 5.0 Hz, 2 × CH$_3$$CH_2$OP), 110.22 (CH$_{Ar}$), 118.80 (d, $^1J_{CP}$ = 184.7 Hz, PC), 120.29 (CH$_{Ar}$), 134.01 (d, $^2J_{CP}$ = 8.0 Hz, CHAr), 149.26 (d, $^3J_{CP}$ = 23.9 Hz, C$_{Ar}$), 157.50 (C$_{Ar}$), 167.17 (d, $^2J_{CP}$ = 11.8 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 15.47.

Anal. Calcd for $C_{12}H_{17}O_6P$: C, 50.00; H, 5.94. Found: C, 49.88; H, 5.85.

(*E*,*Z*)-2-(Diethoxyphosphoryl)-4-methyl-2-pentenoic Acid (3j)
Yield: 95%; colorless oil.

IR (CCl_4): 2776, 1712, 1624, 1392, 1208, 1032, 812, 732 cm^{-1}.

^1H NMR (250 MHz, acetone-d_6): δ = 1.07 [d, $^3J_{HH}$ = 6.8 Hz, 6 H, (CH_3)$_2$CH, *E* isomer], 1.08 [d, $^3J_{HH}$ = 6.5 Hz, 6 H, (CH_3)$_2$CH, *Z* isomer], 1.29 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 × CH_3CH$_2$OP), 3.03–3.25 [m, 1 H, (CH$_3$)$_2$CH, *E* isomer], 3.30–3.45 [m, 1 H, (CH$_3$)$_2$CH, *Z* isomer], 4.04–4.15 (m, 4 H, 2 × CH$_3$CH_2OP), 6.77 (dd, $^3J_{HP}$ = 23.0 Hz, $^3J_{HH}$ = 10.0 Hz, 1 H, C=CH, *E* isomer), 7.44 (dd, $^3J_{HP}$ = 41.8 Hz, $^3J_{HH}$ = 11.8 Hz, 1 H, C=CH, *Z* isomer).

^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 15.68 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH$_3$CH$_2$OP, *E* isomer), 15.70 (d, $^3J_{CP}$ = 6.3 Hz, 2 × CH$_3$CH$_2$OP, *Z* isomer), 21.11 (d, $^4J_{CP}$ = 1.5 Hz, 2 × CH$_3$, *Z* isomer), 21.25 (d, $^4J_{CP}$ = 1.1 Hz, 2 × CH$_3$, *E* isomer), 29.21 [d, $^3J_{CP}$ = 5.0 Hz, (CH$_3$)$_2$$C$H, *Z* isomer], 29.59 [d, $^3J_{CP}$ = 16.3 Hz, (CH$_3$)$_2$$C$H, *E* isomer], 62.50 (d, $^2J_{CP}$ = 5.6 Hz, 2 × CH$_3$$CH_2$OP, *E* isomer), 62.59 (d, $^2J_{CP}$ = 5.8 Hz, 2 × CH$_3$$CH_2$OP, *Z* isomer), 119.38 (d, $^1J_{CP}$ = 184.7 Hz, PC, *Z* isomer), 121.77 (d, $^1J_{CP}$ = 183.6 Hz, PC, *E* isomer), 165.63 (d, $^2J_{CP}$ = 4.0 Hz, C=CH, *E* isomer), 165.81 (d, $^2J_{CP}$ = 18.9 Hz, COOH, *Z* isomer), 166.09 (d, $^2J_{CP}$ = 14.4 Hz, COOH, *E* isomer), 170.83 (d, $^2J_{CP}$ = 7.9 Hz, C=CH, *Z* isomer).

^{31}P NMR (101 MHz, acetone-d_6): δ = 15.09, 16.27 for *E* and *Z* isomers, respectively (*E*:*Z* = 6:1).

Anal. Calcd for $C_{10}H_{19}O_5P$: C, 48.00; H, 7.65. Found: C, 47.89; H, 7.57.

(*E*,*Z*)-3-Cyclohexyl-2-(diethoxyphosphoryl)acrylic Acid (3k)
Yield: 94%; white crystals; mp 64–66 °C.

IR (CCl_4): 2928, 1720, 1612, 1448, 1392, 1200, 1028, 972, 804 cm^{-1}.

^1H NMR (250 MHz, acetone-d_6): δ = 1.19–1.35 (m, 5 H, CH$_2$), 1.29 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 × CH_3CH$_2$OP), 1.71–1.76 (m, 5 H, CH$_2$), 2.89–3.00 [m, 1 H, (CH$_2$)$_5$CH, *E* isomer], 2.99–3.17 [m, 1 H, (CH$_2$)$_5$CH, *Z* isomer], 4.04–4.15 (m, 4 H, 2 × CH$_3$CH_2OP), 6.70 (dd, $^3J_{HP}$ = 23.5 Hz, $^3J_{HH}$ = 10.0 Hz, C=CH, 1 H, *E* isomer), 7.35 (dd, $^3J_{HP}$ = 43.8 Hz, $^3J_{HH}$ = 11.2 Hz, 1 H, C=CH, *Z* isomer).

^{13}C NMR (62.9 MHz, acetone-d_6, *E* isomer): δ = 16.07 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH$_3$CH$_2$OP), 25.04 (2 × CH$_2$), 25.55 (CH$_2$), 31.50 (2 × CH$_2$), 39.57 [d, $^3J_{CP}$ = 15.7 Hz, (CH$_2$)$_5$$C$H], 62.84 (d, $^2J_{CP}$ = 5.6 Hz, 2 × CH$_3$$CH_2$OP), 122.13 (d, $^1J_{CP}$ = 183.29 Hz, PC), 165.07 (C=CH), 166.77 (d, $^2J_{CP}$ = 16.2 Hz, COOH).

^{31}P NMR (101 MHz, acetone-d_6): δ = 15.98, 16.54 for *E* and *Z* isomers, respectively (*E*:*Z* = 95:5).

Anal. Calcd for $C_{13}H_{23}O_5P$: C, 53.79; H, 7.99. Found: C, 53.65; H, 7.88.

Diethyl (*E*)-2-Arylvinylphosphonates (5); General Procedure
A mixture of 2-(diethoxyphosphoryl)acrylic acid **3** (1 mmol) and piperidine (34 mg, 0.4 mmol) in toluene (20 mL) was heated at reflux for 2 h. The solvent was evaporated and the residue was dissolved in CH_2Cl_2 (15 mL), washed with sat. aq $NaHCO_3$ solution (10 mL) and H_2O (10 mL) and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product which was purified by column chromatography [silica gel; CH_2Cl_2–MeOH (98:2) as eluent] to give pure vinylphosphonate **5**.

Diethyl (*E*)-2-(4-Nitrophenyl)vinylphosphonate (5a)[7a]
Yield: 89%; pale yellow crystals; mp 101–103 °C (Lit. 102–103.5 °C).

IR (CCl_4): 2992, 1720, 1612, 1448, 1392, 1200, 1028, 972, 804 cm^{-1}.

^1H NMR (250 MHz, CDCl$_3$): δ = 1.38 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 4.12–4.24 (m, 4 H, 2 × CH$_3$CH_2OP), 6.45 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 16.2 Hz, 1 H, CHP), 7.54 (dd, $^3J_{HP}$ = 22.2 Hz, $^3J_{HH}$ = 17.5 Hz, 1 H, CHAr), 7.67 (d, $^3J_{HH}$ = 8.9 Hz, 2 H, 2 × CH$_{Ar}$), 8.26 (d, $^3J_{HH}$ = 8.9 Hz, 2 H, 2 × CH$_{Ar}$).

^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 16.06 (d, $^3J_{CP}$ = 6.3 Hz, 2 × CH$_3$CH$_2$OP), 61.83 (d, $^2J_{CP}$ = 5.7 Hz, 2 × CH$_3$$CH_2$OP), 119.21 (d, $^1J_{CP}$ = 190.0 Hz, PCH), 123.76 (2 × CH$_{Ar}$), 128.06 (2 × CH$_{Ar}$), 140.55 (d, $^3J_{CP}$ = 23.5 Hz, C$_{Ar}$), 145.13 (d, $^2J_{CP}$ = 6.6 Hz, CHAr), 148.10 (C$_{Ar}$).

^{31}P NMR (101 MHz, CDCl$_3$): δ = 17.52.

Diethyl (*E*)-2-(3-Nitrophenyl)vinylphosphonate (5b)
Yield: 83%; pale yellow crystals; mp 44–46 °C.

IR (CCl_4): 2984, 1624, 1532, 1352, 1236, 1028, 816, 736 cm^{-1}.

^1H NMR (250 MHz, CDCl$_3$): δ = 1.38 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 4.11–4.27 (m, 4 H, 2 × CH$_3$CH_2OP), 6.43 (dd, $^3J_{HH}$ = 17.8 Hz, $^2J_{HP}$ = 16.3 Hz, 1 H, CHP), 7.54 (dd, $^3J_{HP}$ = 21.5 Hz, $^3J_{HH}$ = 17.8 Hz, 1 H, CHAr), 7.59 (t, $^3J_{HH}$ = 8.2 Hz, 1 H, CH$_{Ar}$), 7.89 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH$_{Ar}$), 8.23 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH$_{Ar}$), 8.37 (s, 1 H, CH$_{Ar}$).

^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 16.03 (d, $^3J_{CP}$ = 6.3 Hz, 2 × CH$_3$CH$_2$OP), 61.74 (d, $^2J_{CP}$ = 5.6 Hz, 2 × CH$_3$$CH_2$OP), 117.81 (d, $^1J_{CP}$ = 190.2 Hz, PCH), 121.59 (CH$_{Ar}$), 124.06 (CH$_{Ar}$), 129.66 (CH$_{Ar}$), 133.13 (CH$_{Ar}$), 136.25 (d, $^3J_{CP}$ = 24.0 Hz, C$_{Ar}$), 145.15 (d, $^2J_{CP}$ = 6.9 Hz, CHAr), 148.26 (C$_{Ar}$).

^{31}P NMR (101 MHz, CDCl$_3$): δ = 17.75.

Anal. Calcd for $C_{12}H_{16}NO_5P$: C, 50.63; H, 5.65. Found: C, 50.88; H, 5.73.

Diethyl (*E*)-2-(*p*-Tolyl)vinylphosphonate (5c)[7a]
Yield: 80%; yellow oil.

IR (CCl_4): 2984, 1616, 1512, 1248, 1028, 964, 840, 800 cm^{-1}.

^1H NMR (250 MHz, CDCl$_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH$_2$OP), 2.37 (s, 3 H, CH$_3$Ar), 4.08–4.17 (m, 4 H, 2 × CH$_3$CH_2OP), 6.19 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 17.5 Hz, 1 H, CHP), 7.18 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2 × CH$_{Ar}$), 7.39 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2 × CH_{Ar}), 7.48 (dd, $^3J_{HP}$ = 22.5 Hz, $^3J_{HH}$ = 17.5 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, CDCl$_3$): δ = 15.97 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH$_3$CH$_2$OP), 20.93 (CH$_3$Ar), 61.27 (d, $^2J_{CP}$ = 5.4 Hz, 2 × CH$_3$$CH_2$OP), 112.24 (d, $^1J_{CP}$ = 191.8 Hz, PCH), 127.24 (2 × CH$_{Ar}$), 129.13 (2 × CH$_{Ar}$), 131.73 (d, $^3J_{CP}$ = 23.6 Hz, C$_{Ar}$), 140.11 (C$_{Ar}$), 148.25 (d, $^2J_{CP}$ = 6.7 Hz, CHAr).

^{31}P NMR (101 MHz, CDCl$_3$): δ = 20.34.

Diethyl (*E*)-2-(4-Methoxyphenyl)vinylphosphonate (5d)[7b]
Yield: 84%; yellow oil.

IR (CCl_4): 2984, 1604, 1512, 1304, 1260, 1176, 1024, 964, 864, 848 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.3 Hz, 6 H, 2 × CH_3CH_2OP), 3.84 (s, 3 H, CH_3OAr), 4.03–4.18 (m, 4 H, 2 × CH_3CH_2OP), 6.09 (dd, $^3J_{HH}$ = 17.8 Hz, $^2J_{HP}$ = 17.8 Hz, 1 H, CHP), 6.90 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}), 7.45 (d, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 × CH_{Ar}), 7.45 (dd, $^3J_{HP}$ = 23.5 Hz, $^3J_{HH}$ = 17.8 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.83 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH_3CH_2OP), 54.71 (CH_3OAr), 61.07 (d, $^2J_{CP}$ = 5.4 Hz, 2 × CH_3CH_2OP), 110.40 (d, $^1J_{CP}$ = 192.7 Hz, PCH), 113.68 (2 × CH_{Ar}), 127.03 (d, $^3J_{CP}$ = 23.7 Hz, C_{Ar}), 128.73 (2 × CH_{Ar}), 147.75 (d, $^2J_{CP}$ = 6.9 Hz, CHAr), 160.79 (C_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 20.76.

Diethyl (*E*)-2-(3,4-Dimethoxyphenyl)vinylphosphonate (5e)
Yield: 81%; yellow oil.

IR (CCl_4): 2984, 1600, 1512, 1464, 1268, 1160, 1024, 964, 856, 804 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.36 (t, $^3J_{HH}$ = 7.2 Hz, 6 H, 2 × CH_3CH_2OP), 3.91 (s, 6 H, 2 × CH_3OAr), 4.06–4.19 (m, 4 H, 2 × CH_3CH_2OP), 6.09 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 17.5 Hz, 1 H, CHP), 6.87 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH_{Ar}), 7.03 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, CH_{Ar}), 7.08 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.0 Hz, 1 H, CH_{Ar}), 7.44 (dd, $^3J_{HP}$ = 22.5 Hz, $^3J_{HH}$ = 17.5 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.05 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH_3CH_2OP), 55.51 (CH_3OAr), 55.58 (CH_3OAr), 61.35 (d, $^2J_{CP}$ = 5.4 Hz, 2 × CH_3CH_2OP), 109.05 (CH_{Ar}), 110.67 (CH_{Ar}), 110.86 (d, $^1J_{CP}$ = 192.9 Hz, PCH), 121.76 (CH_{Ar}), 127.53 (d, $^3J_{CP}$ = 23.9 Hz, C_{Ar}), 148.21 (d, $^2J_{CP}$ = 6.9 Hz, CHAr), 148.56 (C_{Ar}), 150.69 (C_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 20.59.

Anal. Calcd for $C_{14}H_{21}O_5P$: C, 56.00; H, 7.05. Found: C, 56.16; H, 7.14.

Diethyl (*E*)-2-(Benzo[1,3]dioxol-5-yl)vinylphosphonate (5f)
Yield: 81%; pale yellow oil.

IR (CCl_4): 2984, 1616, 1492, 1448, 1256, 1032, 964, 800 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, 2 × CH_3CH_2OP), 4.05–4.19 (m, 4 H, 2 × CH_3CH_2OP), 6.01 (s, 2 H, CH_2O_2Ar), 6.05 (dd, $^3J_{HH}$ = 17.4 Hz, $^2J_{HP}$ = 17.4 Hz, 1 H, CHP), 6.81 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, CH_{Ar}), 6.98 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, CH_{Ar}), 7.01 (d, $^4J_{HH}$ = 1.5 Hz, 1 H, CH_{Ar}), 7.40 (dd, $^3J_{HP}$ = 22.4 Hz, $^3J_{HH}$ = 17.4 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.01 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH_3CH_2OP), 61.34 (d, $^2J_{CP}$ = 5.5 Hz, 2 × CH_3CH_2OP), 101.20 (CH_2O_2Ar), 105.78 (CH_{Ar}), 108.02 (CH_{Ar}), 111.09 (d, $^1J_{CP}$ = 192.5 Hz, PCH), 123.54 (CH_{Ar}), 128.94 (d, $^3J_{CP}$ = 24.0 Hz, C_{Ar}), 147.92 (d, $^2J_{CP}$ = 5.7 Hz, CHAr), 147.97 (C_{Ar}), 149.14 (C_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 20.41.

Anal. Calcd for $C_{13}H_{17}O_5P$: C, 54.93; H, 6.03. Found: C, 55.08; H, 6.10.

Diethyl (*E*)-2-(4-Bromophenyl)vinylphosphonate (5g)[3c]
Yield: 82%; white crystals; mp 71–73 °C (Lit. 69–70 °C).

IR (CCl_4): 2984, 1616, 1488, 1396, 1248, 1028, 964, 760 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.36 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH_2OP), 4.08–4.20 (m, 4 H, 2 × CH_3CH_2OP), 6.25 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 17.5 Hz, 1 H, CHP), 7.44 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2 × CH_{Ar}), 7.44 (dd, $^3J_{HP}$ = 22.8 Hz, $^3J_{HH}$ = 17.5 Hz, 1 H, CHAr), 7.52 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2 × CH_{Ar}).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.11 (d, $^3J_{CP}$ = 6.5 Hz, 2 × CH_3CH_2OP), 61.58 (d, $^2J_{CP}$ = 5.5 Hz, 2 × CH_3CH_2OP), 114.72 (d, $^1J_{CP}$ = 191.2 Hz, PCH), 124.10 (C_{Ar}), 128.80 (2 × CH_{Ar}), 131.74 (2 × CH_{Ar}), 133.46 (d, $^3J_{CP}$ = 23.7 Hz, C_{Ar}), 146.86 (d, $^2J_{CP}$ = 6.8 Hz, CHAr).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 19.22.

Diethyl (*E*)-2-(Furan-2-yl)vinylphosphonate (5h)[2d,n]
Yield: 86%; red oil.

IR (CCl_4): 2984, 1624, 1552, 1476, 1392, 1248, 1048, 960, 848, 812, 768 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.2 Hz, 6 H, 2 × CH_3CH_2OP), 4.06–4.17 (m, 4 H, 2 × CH_3CH_2OP), 6.11 (dd, $^3J_{HH}$ = 17.8 Hz, $^2J_{HP}$ = 17.8 Hz, 1 H, CHP), 6.45 (dd, $^3J_{HH}$ = 3.0 Hz, $^3J_{HH}$ = 1.5 Hz, 1 H, CH_{Ar}), 6.55 (d, $^3J_{HH}$ = 3.0 Hz, 1 H, CH_{Ar}), 7.26 (dd, $^3J_{HP}$ = 22.5 Hz, $^3J_{HH}$ = 17.8 Hz, 1 H, CHAr), 7.46 (d, $^3J_{HH}$ = 1.5 Hz, 1 H, CH_{Ar}).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.90 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH_3CH_2OP), 61.35 (d, $^2J_{CP}$ = 5.5 Hz, 2 × CH_3CH_2OP), 110.75 (d, $^1J_{CP}$ = 194.0 Hz, PCH), 111.73 (CH_{Ar}), 113.54 (CH_{Ar}), 134.76 (d, $^2J_{CP}$ = 7.6 Hz, CHAr), 144.16 (CH_{Ar}), 150.56 (d, $^2J_{CP}$ = 25.8 Hz, C_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 19.93.

Diethyl (*E*)-2-(5-Methylfuran-2-yl)vinylphosphonate (5i)[2d]
Yield: 77%; red oil.

IR (CCl_4): 2984, 1624, 1580, 1392, 1248, 1028, 968, 848, 792 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.34 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH_2OP), 2.34 (s, 3 H, CH_3Ar), 4.04–4.16 (m, 4 H, 2 × CH_3CH_2OP), 6.00 (dd, $^3J_{HH}$ = 17.2 Hz, $^3J_{HP}$ = 19.0 Hz, 1 H, CHAr), 6.05 (d, $^3J_{HH}$ = 3.2 Hz, 1 H, CH_{Ar}), 6.44 (d, $^3J_{HH}$ = 3.2 Hz, 1 H, CH_{Ar}), 7.18 (dd, $^3J_{HH}$ = 17.2 Hz, $^2J_{HP}$ = 5.0 Hz, 1 H, CHP).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.48 (CH_3Ar), 16.09 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH_3CH_2OP), 61.38 (d, $^2J_{CP}$ = 5.3 Hz, 2 × CH_3CH_2OP), 108.36 (CH_{Ar}), 108.66 (d, $^1J_{CP}$ = 194.7 Hz, PCH), 115.33 (CH_{Ar}), 133.28 (d, $^2J_{CP}$ = 7.7 Hz, CHAr), 147.70 (d, $^2J_{CP}$ = 25.7 Hz, C_{Ar}), 154.87 (C_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 20.74.

Diethyl (*E*)-2-Arylvinylphosphonates (7); General Procedure
A mixture of diethylphosphonoacetic acid (**1**; 392 mg, 2 mmol), aldehyde **6** (2.4 mmol), piperidine (46 mg, 0.54 mmol) and AcOH (24 mg, 0.4 mmol) in toluene (20 mL) was heated at reflux for 20 h. The reaction progress was occasionally monitored with ^{31}P NMR. After the acid **1** was completely consumed the solvent was evaporated and the residue was taken up in CH_2Cl_2 (15 mL), washed with sat. aq $NaHCO_3$ solution (10 mL), H_2O (10 mL) and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded the crude product, which was purified by column chromatography (silica gel; CH_2Cl_2–MeOH, 98:2 as eluent) to give pure vinylphosphonate **7**.

Diethyl (*E*)-2-(4-Hydroxyphenyl)vinylphosphonate (7a)
Yield: 82%; pale yellow oil.

IR (CCl_4): 2980, 1604, 1512, 1208, 1168, 1024, 964, 808 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH_2OP), 4.07–4.18 (m, 4 H, 2 × CH_3CH_2OP), 6.05 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 17.5 Hz, 1 H, CHP), 6.91 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2 × CH_{Ar}), 7.35 (d, $^3J_{HH}$ = 8.5 Hz, 2 H, 2 × CH_{Ar}), 7.42 (dd, $^3J_{HP}$ = 22.9 Hz, $^3J_{HH}$ = 17.5 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.20 (d, $^3J_{CP}$ = 6.5 Hz, 2 × CH_3CH_2OP), 62.05 (d, $^2J_{CP}$ = 5.5 Hz, 2 × CH_3CH_2OP), 108.14 (d, $^1J_{CP}$ = 194.9 Hz, PCH), 115.97 (2 × CH_{Ar}), 125.98 (d, $^3J_{CP}$ = 23.8

Hz, C_{Ar}), 129.50 (2 × CH_{Ar}), 149.65 (d, $^2J_{CP}$ = 6.9 Hz, CHAr), 159.82 (C_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 21.41.

Anal. Calcd for $C_{12}H_{17}O_4P$: C, 56.25; H, 6.69. Found: C, 56.10; H, 6.60.

Diethyl (*E*)-2-(3-Hydroxyphenyl)vinylphosphonate (7b)
Yield: 68%; yellow oil.

IR (CCl_4): 2980, 1588, 1452, 1292, 1240, 1040, 856, 780 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 × CH_3CH_2OP), 4.08–4.21 (m, 4 H, 2 × CH_3CH_2OP), 6.24 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 17.5 Hz, 1 H, CHP), 6.92 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 7.05 (d, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 7.18 (s, 1 H, CH_{Ar}), 7.21 (t, $^3J_{HH}$ = 8.0 Hz, 1 H, CH_{Ar}), 7.51 (dd, $^3J_{HP}$ = 23.0 Hz, $^3J_{HH}$ = 17.5 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.33 (d, $^3J_{CP}$ = 6.4 Hz, 2 × CH_3CH_2OP), 62.30 (d, $^2J_{CP}$ = 5.5 Hz, 2 × CH_3CH_2OP), 112.57 (d, $^1J_{CP}$ = 191.6 Hz, PCH), 114.99 (CH_{Ar}), 118.15 (CH_{Ar}), 118.80 (CH_{Ar}), 129.93 (CH_{Ar}), 135.70 (d, $^3J_{CP}$ = 23.5 Hz, C_{Ar}), 149.92 (d, $^2J_{CP}$ = 6.5 Hz, CHAr), 157.87 (C_{Ar}).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 20.20.

Anal. Calcd for $C_{12}H_{17}O_4P$: C, 56.25; H, 6.69. Found: C, 56.08; H, 6.62.

Diethyl (*E*)-2-(4-Hydroxy-3-methoxyphenyl)vinylphosphonate (7c)
Yield: 80%; white crystals; mp 99–101 °C.

IR (CCl_4): 2936, 1584, 1512, 1216, 1032, 968, 840, 760 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.1 Hz, 6 H, 2 × CH_3CH_2OP), 3.92 (s, 3 H, CH_3OAr), 4.10–4.18 (m, 4 H, 2 × CH_3CH_2OP), 6.06 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 17.5 Hz, 1 H, CHP), 6.91 (d, $^3J_{HH}$ = 8.1 Hz, 1 H, CH_{Ar}), 7.00 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, CH_{Ar}), 7.05 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, CH_{Ar}), 7.42 (dd, $^3J_{HP}$ = 22.5 Hz, $^3J_{HH}$ = 17.5 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 15.98 (d, $^3J_{CP}$ = 6.5 Hz, 2 × CH_3CH_2OP), 55.50 (CH_3OAr), 61.57 (d, $^2J_{CP}$ = 5.5 Hz, 2 × CH_3CH_2OP), 109.10 (d, $^1J_{CP}$ = 194.1 Hz, PCH), 109.48 (CH_{Ar}), 114.92 (CH_{Ar}), 122.03 (CH_{Ar}), 126.41 (d, $^3J_{CP}$ = 23.8 Hz, C_{Ar}), 147.26 (C_{Ar}), 148.68 (C_{Ar}), 149.03 (d, $^2J_{CP}$ = 6.9 Hz, CHAr).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 20.71.

Anal. Calcd for $C_{13}H_{19}O_5P$: C, 54.54; H, 6.69. Found: C, 54.41; H, 6.60.

Diethyl (*E*)-2-(3,4-Dihydroxyphenyl)vinylphosphonate (7d)
Yield: 79%; white crystals; mp 87–89 °C.

IR (CCl_4): 2992, 1596, 1528, 1444, 1368, 1292, 1188, 1048, 976, 952, 784 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.35 (t, $^3J_{HH}$ = 7.5 Hz, 6 H, 2 × CH_3CH_2OP), 4.06–4.18 (m, 4 H, 2 × CH_3CH_2OP), 6.04 (dd, $^3J_{HH}$ = 17.4 Hz, $^2J_{HP}$ = 19.2 Hz, 1 H, CHP), 6.90 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH_{Ar}), 6.98 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.0 Hz, 1 H, CH_{Ar}), 7.18 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, CH_{Ar}), 7.43 (dd, $^3J_{HP}$ = 23.0 Hz, $^3J_{HH}$ = 17.4 Hz, 1 H, CHAr).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.09 (d, $^3J_{CP}$ = 6.7 Hz, 2 × CH_3CH_2OP), 62.28 (d, $^2J_{CP}$ = 5.6 Hz, 2 × CH_3CH_2OP), 107.87 (d, $^1J_{CP}$ = 195.3 Hz, PCH), 114.21 (CH_{Ar}), 115.42 (CH_{Ar}), 121.32 (CH_{Ar}), 126.73 (d, $^3J_{CP}$ = 24.0 Hz, C_{Ar}), 144.84 (C_{Ar}), 147.60 (C_{Ar}), 150.24 (d, $^2J_{CP}$ = 6.5 Hz, CHAr).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 21.33.

Anal. Calcd for $C_{12}H_{17}O_5P$: C, 52.94; H, 6.29. Found: C, 53.08; H, 6.40.

Diethyl (*E*)-2-(1*H*-Indol-3-yl)vinylphosphonate (7e)
Yield: 76%; brown oil.

IR (CCl_4): 2984, 1608, 1440, 1392, 1216, 1024, 960, 856, 800, 744 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.42 (t, $^3J_{HH}$ = 7.2 Hz, 6 H, 2 × CH_3CH_2OP), 4.14–4.26 (m, 4 H, 2 × CH_3CH_2OP), 6.20 (dd, $^3J_{HH}$ = 17.5 Hz, $^2J_{HP}$ = 18.5 Hz, 1 H, CHP), 7.26–7.35 (m, 2 H, 2 × CH_{Ar}), 7.48–7.51 (m, 2 H, 2 × CH_{Ar}), 7.77 (dd, $^3J_{HP}$ = 23.2 Hz, $^3J_{HH}$ = 17.5 Hz, 1 H, CHAr), 7.93–7.97 (m, 1 H, CH_{Ar}), 9.08 (s, 1 H, NH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 16.22 (d, $^3J_{CP}$ = 6.7 Hz, 2 × CH_3CH_2OP), 61.65 (d, $^2J_{CP}$ = 5.4 Hz, 2 × CH_3CH_2OP), 105.28 (d, $^1J_{CP}$ = 194.6 Hz, PCH), 112.22 (CH_{Ar}), 113.02 (d, $^3J_{CP}$ = 25.6 Hz, C_{Ar}), 119.65 (CH_{Ar}), 120.93 (CH_{Ar}), 122.67 (CH_{Ar}), 124.98 (C_{Ar}), 129.61 (CH_{Ar}), 137.47 (C_{Ar}), 143.40 (d, $^2J_{CP}$ = 6.7 Hz, CHAr).

^{31}P NMR (101 MHz, $CDCl_3$): δ = 22.59.

Anal. Calcd for $C_{14}H_{18}NO_3P$: C, 60.21; H, 6.50. Found: C, 60.41; H, 6.61.

Diethyl Vinylphosphonate (9)[16]
A mixture of the acid **1** (3.92 g, 0.02 mol), dicyclohexylamine (0.543 g, 0.003 mol), DABCO (0.336 g, 0.003 mol) and paraformaldehyde (1.32 g, 0.044 mol) in benzene (50 mL) was heated at reflux under a Dean–Stark water separator for 2 h. The solution was filtered to remove the polymeric species and the filtrate was concentrated under vacuum. The resulting oily residue was dissolved in $CHCl_3$ (50 mL), washed with water (3 × 10 mL) and dried over $MgSO_4$. Removal of the solvent gave the crude product, which was purified by vacuum distillation. Yield: 73%; colorless oil; bp 80–82 °C/15 mmHg (lit.[16b] bp 80–83/15 mmHg).

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