Bromodecarboxylation of (*E*)-3-Aryl-2-(diethoxyphosphoryl)acrylic Acids: A Facile Route to Diethyl Arylethynylphosphonates

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Abstract: Bromodecarboxylation of (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids leading to diethyl (*Z*)-2-aryl-1-bromovinylphosphonates has been conducted for the first time. The products have been shown to be useful for the synthesis of diethyl arylethynylphosphonates.

Key words: Hunsdiecker reaction, bromodecarboxylation, alk-1-ynylphosphonates, Oxone, acrylic acids

Decarboxylation of carboxylic acids accompanied by simultaneous replacement by a halogen, known in the literature as the Hunsdiecker reaction, constitutes an important and useful method for the synthesis of halogenated organic compounds containing one fewer carbon atom than the original acid.[1] It is well established that simple alkanoic acids can be converted into the corresponding alkyl bromides by reaction of their silver salts with elemental bromine. Unfortunately, the salts of α,β-unsaturated acids were found not to be useful in this reaction.[1] Recently, the Hunsdiecker reaction of cinnamic acids has been shown to proceed efficiently in the presence of various reagents (NBS/iodosylbenzene,[2a] NBS/LiOAc,[2b] NBS/LiOAc with irradiation,[2c] tetrabutylammonium trifluoroacetate/*N*-halosuccinimides,[2d] NaX/Oxone,[2e] KBr/Selectfluor,[2f] $KBr/Na_2MoO_4{\cdot}2H_2O/H_2O_2$,[2g] Dess–Martin periodinane/TEAB,[2h] LiBr/CAN[2i]) giving access to a range of vinyl halides.

Halogen-substituted vinylphosphonates are masked acetylenic compounds as they can be easily transformed into the corresponding alk-1-ynylphosphonates.[3] Moreover, 1-bromoalk-1-enylphosphonates have been successfully utilized for the preparation of the corresponding 1-arylalk-1-enylphosphonates and phosphorylated dienes by means of transition-metal-catalyzed arylation and alkenylation.[4] 1-Bromoalk-1-enylphosphonates are commonly prepared through a sequence of reactions involving addition of elemental bromine to alk-1-enylphosphonates and base-catalyzed β-elimination of the resulting 1,2-dibromoalkylphosphonates.[4,5] These reactions lead to the formation of particular products as mixtures of *E*- and *Z*-isomers. For this reason, methods to obtain such compounds in a stereoselective manner are desirable.

Alk-1-ynylphosphonates have found widespread application in organic synthesis.[6] Stereoselective partial reduction of the triple bond of dibutyl prop-1-ynylphosphonate to give dibutyl (*Z*)-prop-1-enylphosphonate constitutes a key step in the first racemic synthesis of the antibiotic fosfomycin.[7] Hydration of alk-1-ynylphosphonates provides an effective and general approach for the preparation of 2-oxoalkylphosphonates, versatile synthetic intermediates.[8] Additionally, alk-1-ynylphosphonates have been utilized in [2+2]-, [3+2]-, and [4+2]-cycloaddition reactions for the synthesis of complex organophosphorus compounds.[6] Alk-1-ynylphosphonates are also useful precursors for the preparation of arylidenebisphosphonates providing a new access to the P–C–P backbone.[9] Recently, the reagent system Cp_2ZrCl_2/2 EtMgBr/2 $AlCl_3$ was shown to convert alk-1-ynylphosphonates into cyclopropylmethylphosphonates in good isolated yields.[10] As a consequence considerable effort has been directed towards the development of methods for their simple and effective preparation.[6]

Recently, we have demonstrated that Knoevenagel condensation of (diethoxyphosphoryl)acetic acid with various aromatic aldehydes gives access to a range of (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids **1**.[11] Moreover, we have shown that subsequent decarboxylation of the acids **1** constitutes an efficient and general route to diethyl (*E*)-2-arylvinylphosphonates. We envisioned that Hunsdiecker reaction of the acids **1** would provide a new approach to 1-bromoalk-1-enylphosphonates.

In this paper, we report our results on the bromodecarboxylation of acids **1** using sodium bromide in the presence of Oxone at room temperature. Moreover, we demonstrate that the resulting diethyl 2-aryl-1-bromovinylphosphonates can be easily converted into diethyl arylethynylphosphonates, thus providing a novel approach to this class of compounds.

In our initial studies, we focused on finding a suitable method for the effective bromodecarboxylation of (*E*)-3-aryl-2-(diethoxyphosphoryl)acrylic acids **1** (Scheme 1). (*E*)-2-(Diethoxyphosphoryl)-3-(4-methoxyphenyl)acrylic acid (**1a**) was chosen as a model substrate and various methods for its conversion into alkenyl bromide **2a** were evaluated. The use of lithium bromide in the presence of ammonium cerium(IV) nitrate at room temperature resulted in the formation of a complex reaction mixture. The reaction of the acid **1a** with potassium bromide and hydrogen peroxide in the presence of molybdic acid proceeded rapidly, giving the desired bromide **2a** in moderate

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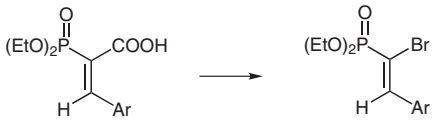
yield and purity. The best results in terms of yield and purity were obtained using sodium bromide in the presence of sodium carbonate and Oxone at room temperature; under these conditions the corresponding alkenyl bromide **2a** was formed in 93% yield. Our investigation on the generality of this methodology showed that electronic effects of the aryl substituent had a profound impact on the reactivity of the substrate. Reactions of 3-aryl-2-(diethoxyphosphoryl)acrylic acids bearing electron-withdrawing group on the aromatic ring proceeded very slowly and were not chemoselective. In practice, this methodology could be efficiently applied to acrylic acids **1a–d** bearing electron-donating groups on the aromatic ring. With the same reagent system, heteroaromatic-substituted acrylic acids **1e**,**f** also provided the respective bromodecarboxylation products **2e**,**f**, but in moderate yield (Table 1).

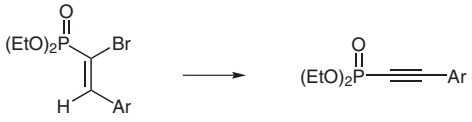


1a–f **2a–f**

Scheme 1 *Reagents and conditions*: KBr (3 equiv), Na_2CO_3 (1 equiv), Oxone (2 equiv), MeCN, H_2O, r.t.

Bromodecarboxylation of the acids **1a–f** proceeded with retention of configuration of the double bond and provided the products as the *Z*-isomer accompanied by a small amount of the *E*-isomer (ratios *Z*/*E* are given in Table 1). Similar results with regard to diastereoselectivity were observed for the bromodecarboxylation of cinnamic acid derivatives.[2c,f,12] The configuration of the alkene bond in bromides **2a–f** was unambiguously assigned on the basis of ^{1}H NMR data; the value of the coupling constant ($^3J_{HP}$ = 15.5–16.3 Hz) indicate a *cis* relationship between vicinal P and H atoms.

With suitable substrates in hand, we turned our attention to their effective conversion into diethyl arylethynylphosphonates **3a–f** (Scheme 2). After much experimentation it was found that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) promoted β-elimination of corresponding alkenyl



2a–f **3a–f**

Scheme 2 *Reagents and conditions*: DBU (1.5 equiv) or TBD (1.2 equiv), CH_2Cl_2, r.t.

bromides **2a–d** proceeded efficiently at room temperature.

Reactions were complete within 6–10 days giving the target phosphonates **3a–d** in high yields. In contrast, the reactions of the heteroaromatic-substituted bromides **2e**,**f** were not chemoselective and led to a mixture of organophosphorus compounds. Much better results in terms of reaction time were obtained using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as a base. Under these conditions reactions of bromides **2a–e** were complete within 1–2 days giving the target phosphonates **3a–e** in comparable yields. Unfortunately, 1,5,7-triazabicyclo[4.4.0]dec-5-ene-promoted elimination of diethyl 2-(1-acetyl-1*H*-indol-3-yl)-1-bromovinylphosphonate (**2f**) resulted in a complex reaction mixture. In all reactions performed, only the *Z*-isomer underwent β-elimination while the *E*-isomer remained unreacted. The pure diethyl arylethynylphosphonates **3a–e** were isolated by column chromatography.

In summary, we have developed a novel and efficient method for the preparation of diethyl 2-aryl-1-bromovinylphosphonates in a highly stereoselective manner. Moreover, we have shown that this type of compound can be successfully used for the synthesis of diethyl arylethynylphosphonates.

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 were 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.

Table 1 2-Aryl-1-bromovinylphosphonates **2a–f** and Arylethynylphosphonates **3a–e** Prepared

Entry	Ar	Vinylphosphonate **2**				Ethynylphosphonate **3**			
		Time (min)	Yield (%)	Ratio *Z*/*E*		DBU-promoted reaction		TBD-promoted reaction	
						Time (d)	Yield (%)	Time (d)	Yield (%)
1	4-$MeOC_6H_4$	**2a**	90	93	94:6	**3a**	7	72	1	75
2	4-MeC_6H_4	**2b**	90	84	95:5	**3b**	8	81	1	80
3	3,4-$(MeO)_2C_6H_3$	**2c**	90	91	96:4	**3c**	10	77	1	81
4	3,4-$(OCH_2O)C_6H_3$	**2d**	90	67	95:5	**3d**	6	73	1	72
5	5-methylfuran-2-yl	**2e**	60	48	98:2	**3e**	–	–	2	60
6	1-acetyl-1H-indol-3-yl	**2f**	60	43	99:1	**3f**	–	–	–	–

Acrylic acids **1a–f** were prepared according to the literature procedure.[11] The synthesis and spectral data of **1f** have not been previously reported.

(*E*)-3-(1-Acetyl-1*H*-indol-3-yl)-2-(diethoxyphosphoryl)acrylic Acid (1f)

Pale-yellow crystals; yield: 51%; mp 136–137 °C.

IR (film): 1716, 1448, 1372, 1330, 1252, 1056, 772 cm^{-1}.

^1H NMR (acetone-d_6): δ = 1.35 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 CH_3CH$_2$OP), 2.71 (s, 3 H, CH_3CO), 4.14–4.25 (m, 4 H, 2 CH$_3$CH_2OP), 7.33–7.45 (m, 2 H, 2 CH_{Ar}), 7.75–7.79 (m, 1 H, CH_{Ar}), 7.90 (d, $^3J_{HP}$ = 23.9 Hz, 1 H, C*H*Ar), 8.38–8.42 (m, 1 H, CH_{Ar}), 8.51 (s, 1 H, CH_{Ar}).

^{13}C NMR (MeOD): δ = 15.82 (d, $^3J_{CP}$ = 6.1 Hz, 2 *C*H$_3$CH$_2$OP), 22.99 (*C*H$_3$CO), 63.52 (d, $^2J_{CP}$ = 5.2 Hz, 2 CH$_3$*C*H$_2$OP), 115.34 (d, $^3J_{CP}$ = 22.2 Hz, C_{Ar}), 116.60 (*C*H$_{Ar}$), 118.28 (*C*H$_{Ar}$), 121.81 (d, $^1J_{CP}$ = 178.9 Hz, P*C*), 124.48 (*C*H$_{Ar}$), 125.88 (*C*H$_{Ar}$), 129.84 (C_{Ar}), 129.96 (*C*H$_{Ar}$), 135.49 (C_{Ar}), 140.19 (d, $^2J_{CP}$ = 7.8 Hz, *C*HAr), 167.73 (d, $^2J_{CP}$ = 11.9 Hz, *C*OOH), 169.91 (CO).

^{31}P NMR (acetone-d_6): δ = 15.11.

Anal. Calcd for $C_{17}H_{20}NO_6P$: C, 55.89; H, 5.52; N, 3.83. Found: C, 55.77; H, 5.43; N, 3.71.

Diethyl 2-Aryl-1-bromovinylphosphonates 2a–f; General Procedure

The soln of Oxone (613 mg, 1 mmol) in H_2O (6 mL) was added dropwise to a mixture of acrylic acid **1** (1 mmol), NaBr (309 mg, 3 mmol), and Na_2CO_3 (106 mg, 1 mmol) in MeCN (9 mL) and H_2O (6 mL). The resulting mixture was stirred at r.t. for the indicated period of time (Table 1). The mixture was then quenched with aq $Na_2S_2O_3$ (15 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The crude product was purified by a column chromatography (EtOAc–hexane 2:1) affording pure **2**.

Diethyl (*Z*)-1-Bromo-2-(4-methoxyphenyl)vinylphosphonate (2a)

Pale-yellow oil; yield: 93%.

IR (film): 1600, 1512, 1256, 1020, 968 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.39 (t, $^3J_{HH}$ = 6.9 Hz, 6 H, 2 CH_3CH$_2$OP), 3.85 (s, 3 H, CH_3OPh), 4.09–4.26 (m, 4 H, 2 CH$_3$CH_2OP), 6.95 (d, $^3J_{HH}$ = 8.9 Hz, 2 H, 2 CH_{Ar}), 7.89 (d, $^3J_{HH}$ = 8.9 Hz, 2 H, 2 CH_{Ar}), 8.00 (d, $^3J_{HP}$ = 16.3 Hz, 1 H, C*H*Ar).

^{13}C NMR ($CDCl_3$): δ = 15.92 (d, $^3J_{CP}$ = 6.5 Hz, 2 *C*H$_3$CH$_2$OP), 54.99 (*C*H$_3$OPh), 62.70 (d, $^2J_{CP}$ = 5.3 Hz, 2 CH$_3$*C*H$_2$OP), 106.15 (d, $^1J_{CP}$ = 208.1 Hz, P*C*Br), 113.51 (2 *C*H$_{Ar}$), 126.04 (d, $^3J_{CP}$ = 18.2 Hz, C_{Ar}), 131.68 (2 *C*H$_{Ar}$), 143.84 (d, $^2J_{CP}$ = 17.1 Hz, *C*HAr), 160.83 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = 11.74.

Anal. Calcd for $C_{13}H_{18}BrO_4P$: C, 44.72; H, 5.20. Found: C, 44.63; H, 5.30.

Diethyl (*Z*)-1-Bromo-2-(4-methylphenyl)vinylphosphonate (2b)

Pale-yellow oil; yield: 84%.

IR (film): 1604, 1440, 1252, 1020, 968 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.39 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.8 Hz, 6 H, 2 CH_3CH$_2$OP), 2.38 (s, 3 H, CH_3Ph), 4.11–4.26 (m, 4 H, 2 CH$_3$CH_2OP), 7.23 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2 CH_{Ar}), 7.76 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2 CH_{Ar}), 8.02 (d, $^3J_{HP}$ = 16.3 Hz, 1 H, C*H*Ar).

^{13}C NMR ($CDCl_3$): δ = 16.25 (d, $^3J_{CP}$ = 6.4 Hz, 2 *C*H$_3$CH$_2$OP), 21.51 (*C*H$_3$Ph), 63.11 (d, $^2J_{CP}$ = 5.2 Hz, 2 CH$_3$*C*H$_2$OP), 108.48 (d, $^1J_{CP}$ = 206.9 Hz, P*C*Br), 129.15 (2 *C*H$_{Ar}$), 130.02 (2 *C*H$_{Ar}$), 131.02 (d, $^3J_{CP}$ = 17.8 Hz, C_{Ar}), 140.66 (C_{Ar}), 144.69 (d, $^2J_{CP}$ = 16.7 Hz, *C*HAr).

^{31}P NMR ($CDCl_3$): δ = 11.65.

Anal. Calcd for $C_{13}H_{18}BrO_3P$: C, 46.87; H, 5.45. Found: C, 46.63; H, 5.30.

Diethyl (*Z*)-1-Bromo-2-(3,4-dimethoxyphenyl)vinylphosphonate (2c)

Yellow oil; yield: 91%.

IR (film): 1596, 1512, 1264, 1144, 1020, 968 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.40 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.8 Hz, 6 H, 2 CH_3CH$_2$OP), 3.92 (s, 3 H, CH_3OAr), 3.93 (s, 3 H, CH_3OAr), 4.11–4.29 (m, 4 H, 2 CH$_3$CH_2OP), 6.91 (d, $^3J_{HH}$ = 8.3 Hz, 1 H, CH_{Ar}), 7.46 (dd, $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 2.0 Hz, 1 H, CH_{Ar}), 7.60 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, CH_{Ar}), 7.99 (d, $^3J_{HP}$ = 16.3 Hz, 1 H, C*H*Ar).

^{13}C NMR ($CDCl_3$): δ = 15.95 (d, $^3J_{CP}$ = 6.9 Hz, 2 *C*H$_3$CH$_2$OP), 55.61 (2 *C*H$_3$OAr), 62.75 (d, $^2J_{CP}$ = 5.2 Hz, 2 CH$_3$*C*H$_2$OP), 106.24 (d, $^1J_{CP}$ = 207.9 Hz, P*C*Br), 110.40 (*C*H$_{Ar}$), 112.19 (*C*H$_{Ar}$), 124.36 (*C*H$_{Ar}$), 126.24 (d, $^3J_{CP}$ = 18.2 Hz, C_{Ar}), 144.00 (d, $^2J_{CP}$ = 17.3 Hz, *C*HAr), 148.20 (C_{Ar}), 150.54 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = 12.04.

Anal. Calcd for $C_{14}H_{20}BrO_5P$: C, 44.35; H, 5.32. Found: C, 44.53; H, 5.21.

Diethyl (*Z*)-1-Bromo-2-[3,4-(methylenedioxy)phenyl]vinylphosphonate (2d)

Pale-yellow oil; yield: 67%.

IR (film): 1592, 1504, 1488, 1448, 1248, 1020, 972 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.39 (dt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HP}$ = 0.3 Hz, 6 H, 2 CH_3CH$_2$OP), 4.09–4.28 (m, 4 H, 2 CH$_3$CH_2OP), 6.03 (s, 2 H, CH_2O$_2$Ar), 6.85 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH_{Ar}), 7.28 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.8 Hz, 1 H, CH_{Ar}), 7.61 (d, $^4J_{HH}$ = 1.8 Hz, 1 H, CH_{Ar}), 7.95 (d, $^3J_{HP}$ = 16.3 Hz, 1 H, C*H*Ar).

^{13}C NMR ($CDCl_3$): δ = 16.00 (d, $^3J_{CP}$ = 6.5 Hz, 2 *C*H$_3$CH$_2$OP), 62.84 (d, $^2J_{CP}$ = 5.1 Hz, 2 CH$_3$*C*H$_2$OP), 101.40 (*C*H$_2$O$_2$Ar), 106.88 (d, $^1J_{CP}$ = 207.6 Hz, P*C*Br), 108.08 (*C*H$_{Ar}$), 108.89 (*C*H$_{Ar}$), 126.15 (*C*H$_{Ar}$), 127.58 (d, $^3J_{CP}$ = 18.3 Hz, C_{Ar}), 143.87 (d, $^2J_{CP}$ = 17.2 Hz, *C*HAr), 147.40 (C_{Ar}), 149.08 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = 11.48.

Anal. Calcd for $C_{13}H_{16}BrO_5P$: C, 43.00; H, 4.44. Found: C, 43.13; H, 4.31.

Diethyl (*Z*)-1-Bromo-2-(5-methylfuran-2-yl)vinylphosphonate (2e)

Yellow oil; yield: 48%.

IR (film): 1616, 1584, 1516, 1252, 1024, 972 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.37 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 CH_3CH$_2$OP), 2.35 (s, 3 H, CH_3Ar), 4.06–4.23 (m, 4 H, 2 CH$_3$CH_2OP), 6.17 (d, $^3J_{HH}$ = 3.3 Hz, 1 H, CH_{Ar}), 7.24 (d, $^3J_{HH}$ = 3.3 Hz, 1 H, CH_{Ar}), 7.90 (d, $^3J_{HP}$ = 15.8 Hz, 1 H, C*H*Ar).

^{13}C NMR ($CDCl_3$): δ = 13.70 (*C*H$_3$Ar), 16.08 (d, $^3J_{CP}$ = 6.6 Hz, 2 *C*H$_3$CH$_2$OP), 62.86 (d, $^2J_{CP}$ = 5.2 Hz, 2 CH$_3$*C*H$_2$OP), 103.54 (d, $^1J_{CP}$ = 211.2 Hz, P*C*Br), 108.72 (*C*H$_{Ar}$), 117.56 (*C*H$_{Ar}$), 132.87 (d, $^2J_{CP}$ = 18.9 Hz, *C*HAr), 148.28 (d, $^3J_{CP}$ = 22.5 Hz, C_{Ar}), 155.10 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = 12.06.

Anal. Calcd for $C_{11}H_{16}BrO_4P$: C, 40.89; H, 4.99. Found: C, 40.73; H, 4.81.

Diethyl (*Z*)-2-(1-Acetyl-1*H*-indol-3-yl)-1-bromovinylphosphonate (2f)
Yellow oil; yield: 43%.

IR (film): 1716, 1448, 1376, 1332, 1252, 1212, 1056, 972 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.41 (dt, $^3J_{HH}$ = 7.0 Hz, $^4J_{HP}$ = 0.5 Hz, 6 H, 2 CH_3CH$_2$OP), 2.73 (s, 3 H, CH_3C(O)N), 4.11–4.29 (m, 4 H, 2 CH$_3$CH_2OP), 7.34–7.47 (m, 2 H, 2 CH_{Ar}), 7.75 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, CH_{Ar}), 8.30 (d, $^3J_{HP}$ = 15.5 Hz, 1 H, C*H*Ar), 8.46 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.2 Hz, 1 H, CH_{Ar}), 8.65 (s, 1 H, CH_{Ar}).

^{13}C NMR ($CDCl_3$): δ = 16.13 (d, $^3J_{CP}$ = 6.5 Hz, 2 *C*H$_3$CH$_2$OP), 23.80 [*C*H$_3$C(O)N], 63.05 (d, $^2J_{CP}$ = 5.2 Hz, 2 CH$_3$*C*H$_2$OP), 110.02 (d, $^1J_{CP}$ = 208.8 Hz, P*C*Br), 116.00 (d, $^3J_{CP}$ = 18.9 Hz, C_{Ar}), 116.42 (*C*H$_{Ar}$), 118.24 (*C*H$_{Ar}$), 124.14 (*C*H$_{Ar}$), 126.02 (*C*H$_{Ar}$), 126.29 (*C*H$_{Ar}$), 129.31 (C_{Ar}), 134.53 (d, $^3J_{CP}$ = 18.6 Hz, *C*HAr), 134.68 (C_{Ar}), 168.51 [*C*(O)N].

^{31}P NMR ($CDCl_3$): δ = 10.76.

Anal. Calcd for $C_{16}H_{19}BrNO_4P$: C, 48.02; H, 4.79; N, 3.50. Found: C, 48.13; H, 4.88; N, 3.59.

Diethyl Arylethynylphosphonates 3a–e; General Procedure
A soln of a corresponding 1-bromovinylphosphonate **2** (1 mmol) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (167 mg, 1.2 mmol) in CH_2Cl_2 (10 mL) was stirred at r.t. for the appropriate period of time (Table 1). The reaction progress was occasionally monitored with ^{31}P NMR. After the bromide **2** was completely reacted the mixture was successively washed with 1 M HCl (10 mL) and H_2O (10 mL) and dried ($MgSO_4$). Evaporation of the solvent under reduced pressure afforded the crude product, which was purified by column chromatography (EtOAc–hexane 2:1) to give pure **3**.

Diethyl 4-Methoxyphenylethynylphosphonate (3a)[3d]
Pale-yellow oil; yield: 75%.

IR (film): 2184, 1604, 1512, 1256, 1028 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.40 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 CH_3CH$_2$OP), 3.84 (s, 3 H, CH_3OPh), 4.17–4.30 (m, 4 H, 2 CH$_3$CH_2OP), 6.88 (d, 2 H, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 CH_{Ar}), 7.51 (d, 2 H, $^3J_{HH}$ = 8.8 Hz, 2 H, 2 CH_{Ar}).

^{13}C NMR ($CDCl_3$): δ = 15.86 (d, $^3J_{CP}$ = 6.9 Hz, 2 *C*H$_3$CH$_2$OP), 55.14 (*C*H$_3$OPh), 62.85 (d, $^2J_{CP}$ = 5.5 Hz, 2 CH$_3$*C*H$_2$OP), 76.86 (d, $^1J_{CP}$ = 302.0 Hz, P*C*), 99.60 (d, $^2J_{CP}$ = 53.8 Hz, *C*Ar), 110.95 (d, $^3J_{CP}$ = 5.7 Hz, C_{Ar}), 114.02 (2 *C*H$_{Ar}$), 134.12 (2 *C*H$_{Ar}$), 161.23 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = –4.74.

Anal. Calcd for $C_{13}H_{17}O_4P$: C, 58.21; H, 6.39. Found: C, 58.09; H, 6.30.

Diethyl 4-Methylphenylethynylphosphonate (3b)[3d]
Pale-yellow oil; yield: 80%.

IR (film): 2184, 1608, 1512, 1264, 1024, 976 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.40 (t, $^3J_{HH}$ = 8.0 Hz, 6 H, 2 CH_3CH$_2$OP), 2.38 (s, 3 H, CH_3Ph), 4.17–4.29 (m, 4 H, 2 CH$_3$CH_2OP), 7.18 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2 CH_{Ar}), 7.46 (d, $^3J_{HH}$ = 8.0 Hz, 2 H, 2 CH_{Ar}).

^{13}C NMR ($CDCl_3$): δ = 15.85 (d, $^3J_{CP}$ = 7.0 Hz, 2 *C*H$_3$CH$_2$OP), 21.40 (*C*H$_3$Ph), 62.91 (d, $^2J_{CP}$ = 5.6 Hz, 2 CH$_3$*C*H$_2$OP), 77.46 (d, $^1J_{CP}$ = 300.8 Hz, P*C*), 99.38 (d, $^2J_{CP}$ = 53.5 Hz, *C*Ar), 116.10 (d, $^3J_{CP}$ = 5.7 Hz, C_{Ar}), 129.09 (2 *C*H$_{Ar}$), 132.27 (2 *C*H$_{Ar}$), 141.10 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = –5.02.

Anal. Calcd for $C_{13}H_{17}O_3P$: C, 61.90; H, 6.79. Found: C, 61.77; H, 6.65.

Diethyl 3,4-Dimethoxyphenylethynylphosphonate (3c)
White crystals; yield: 81%; mp 68–70 °C.

IR (film): 2176, 1600, 1512, 1444, 1252, 1024, 960 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.41 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 CH_3CH$_2$OP), 3.89 (s, 3 H, CH_3OAr), 3.92 (s, 3 H, CH_3OAr), 4.17–4.29 (m, 4 H, 2 CH$_3$CH_2OP), 6.84 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH_{Ar}), 7.04 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, CH_{Ar}), 7.20 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.0 Hz, 1 H, CH_{Ar}).

^{13}C NMR ($CDCl_3$): δ = 15.83 (d, $^3J_{CP}$ = 7.0 Hz, 2 *C*H$_3$CH$_2$OP), 55.67 (2 CH_3OAr), 62.85 (d, $^2J_{CP}$ = 5.5 Hz, 2 CH$_3$*C*H$_2$OP), 76.66 (d, $^1J_{CP}$ = 301.7 Hz, P*C*), 99.57 (d, $^2J_{CP}$ = 53.7 Hz, *C*Ar), 110.82 (*C*H$_{Ar}$), 110.92 (d, $^3J_{CP}$ = 6.0 Hz, C_{Ar}), 114.49 (*C*H$_{Ar}$), 126.43 (*C*H$_{Ar}$), 148.46 (C_{Ar}), 151.22 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = –4.77.

Anal. Calcd for $C_{14}H_{19}O_5P$: C, 56.37; H, 6.42. Found: C, 56.49; H, 6.55.

Diethyl 3,4-(Methylenedioxy)phenylethynylphosphonate (3d)[3d]
Pale-yellow oil; yield: 72%.

IR (film): 2176, 1440, 1252, 1168, 1032, 968 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.40 (t, $^3J_{HH}$ = 7.0 Hz, 6 H, 2 CH_3CH$_2$OP), 4.16–4.28 (m, 4 H, 2 CH$_3$CH_2OP), 6.02 (s, 2 H, CH_2O_2Ar), 6.79 (d, $^3J_{HH}$ = 8.2 Hz, 1 H, CH_{Ar}), 6.97 (d, $^4J_{HH}$ = 1.5 Hz, 1 H, CH_{Ar}), 7.12 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.5 Hz, 1 H, CH_{Ar}).

^{13}C NMR ($CDCl_3$): δ = 15.72 (d, $^3J_{CP}$ = 7.0 Hz, 2 *C*H$_3$CH$_2$OP), 62.77 (d, $^2J_{CP}$ = 5.5 Hz, 2 CH$_3$CH$_2$OP), 76.44 (d, $^1J_{CP}$ = 301.0 Hz, P*C*), 99.02 (d, $^2J_{CP}$ = 53.2 Hz, *C*Ar), 101.48 (*C*H$_2$O$_2$Ar), 108.32 (*C*H$_{Ar}$), 111.56 (*C*H$_{Ar}$), 111.95 (d, $^3J_{CP}$ = 5.8 Hz, C_{Ar}), 127.80 (*C*H$_{Ar}$), 147.24 (C_{Ar}), 149.64 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = –5.04.

Anal. Calcd for $C_{13}H_{15}O_5P$: C, 55.32; H, 5.36. Found: C, 55.23; H, 5.46.

Diethyl 5-Methylfuran-2-ylethynylphosphonate (3e)
Pale-yellow oil; yield: 60%.

IR (film): 2176, 1592, 1528, 1268, 1024 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.40 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.7 Hz, 6 H, 2 CH_3CH$_2$OP), 2.33 (s, 3 H, CH_3Ar), 4.15–4.28 (m, 4 H, 2 CH$_3$CH_2OP), 6.05 (d, $^3J_{HH}$ = 3.4 Hz, 1 H, CH_{Ar}), 6.80 (d, $^3J_{HH}$ = 3.4 Hz, 1 H, CH_{Ar}).

^{13}C NMR ($CDCl_3$): δ = 13.66 (*C*H$_3$Ar), 15.83 (d, $^3J_{CP}$ = 7.1 Hz, 2 *C*H$_3$CH$_2$OP), 63.11 (d, $^2J_{CP}$ = 5.5 Hz, 2 CH$_3$*C*H$_2$OP), 83.07 (d, $^1J_{CP}$ = 297.0 Hz, P*C*), 89.16 (d, $^2J_{CP}$ = 53.9 Hz, *C*Ar), 107.47 (*C*H$_{Ar}$), 121.45 (*C*H$_{Ar}$), 132.46 (d, $^3J_{CP}$ = 6.6 Hz, C_{Ar}), 156.21 (C_{Ar}).

^{31}P NMR ($CDCl_3$): δ = –5.90.

Anal. Calcd for $C_{11}H_{15}O_4P$: C, 54.55; H, 6.24. Found: C, 54.40; H, 6.33.

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