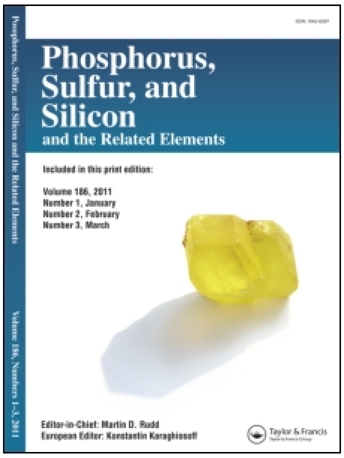

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An Efficient Synthesis of β,γ -Disubstituted α -Diethoxyphosphoryl-γ -lactones: A Convenient Approach to α -Methylene-γ -lactones

Henryk Krawczyk[a]; Łukasz Albrecht[a]
[a] Institute of Organic Chemistry, Technical University (Politechnika), Łódź, Poland

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An Efficient Synthesis of β,γ-Disubstituted α-Diethoxyphosphoryl-γ-lactones: A Convenient Approach to α-Methylene-γ-lactones

Henryk Krawczyk and Łukasz Albrecht
Institute of Organic Chemistry, Technical University (Politechnika), Łódź, Poland

A synthesis of β,γ-disubstituted α-diethoxyphosphoryl-γ-lactones from easily available dicyclohexylammonium 3-aryl-2-diethoxyphosphoryl-4-oxopentanoates is reported. The phosphonolactones were transformed into the corresponding α-methylene-γ-lactones by means of the Horner–Wadsworth–Emmons reaction with formaldehyde.

Keywords α-Alkylidene-γ-lactones; α-diethoxyphosphoryl-γ-lactones; Horner–Wadsworth–Emmons reaction

INTRODUCTION

The α-alkylidene-γ-lactone system is widely distributed in nature, and some derivatives have been shown to exhibit biological and pharmacological activity.[1–8] The α-alkylidene-γ-lactones are also very attractive precursors for a wide variety of compounds, since they can readily undergo reduction,[9–11] oxidation,[12] aziridination,[13] 1,3-dipolar[14,15] and Diels–Alder cycloadditions,[16–18] nucleophilic conjugate additions,[16–18] cross-metathesis reactions,[19,20] and intramolecular Stetter reactions.[21] Therefore a significant effort has been devoted towards development of methods for their simple and efficient preparation. Over the years, several approaches for the synthesis of α-alkylidene-γ-lactones have been reported.[22–37]

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Dedicated to Professor Marian Mikołajczyk from the CBMiM PAN in Łódź, Poland, on the occasion of his 70th birthday.
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Address correspondence to Henryk Krawczyk, Institute of Organic Chemistry, Technical University (Politechnika), Żeromskiego 116, 90-924 Łódź, Poland. E-mail: henkrawc@p.lodz.pl

Recently, we have been involved in the chemistry of α-diethoxyphosphoryl-γ-[38–40] and δ-lactones.[41–46] In our previous work we have reported the synthesis of β- and γ-monosubstituted α-diethoxyphosphoryl-γ-lactones.[38–40] We have also demonstrated that the Horner—Wadsworth–Emmons reaction of the corresponding α-diethoxyphosphoryl-γ-lactones with formaldehyde constitutes a useful method for the preparation of α-methylene-γ-lactones.[38] Moreover, we have discovered that α-diethoxyphosphoryl-γ-lactones can be successfully used as starting materials for the preparation of ethyl cyclopropanecarboxylates.[39–40] We have come to the conclusion that both of these methodologies would significantly benefit from the availability of functionalized α-diethoxyphosphoryl-γ-lactones.

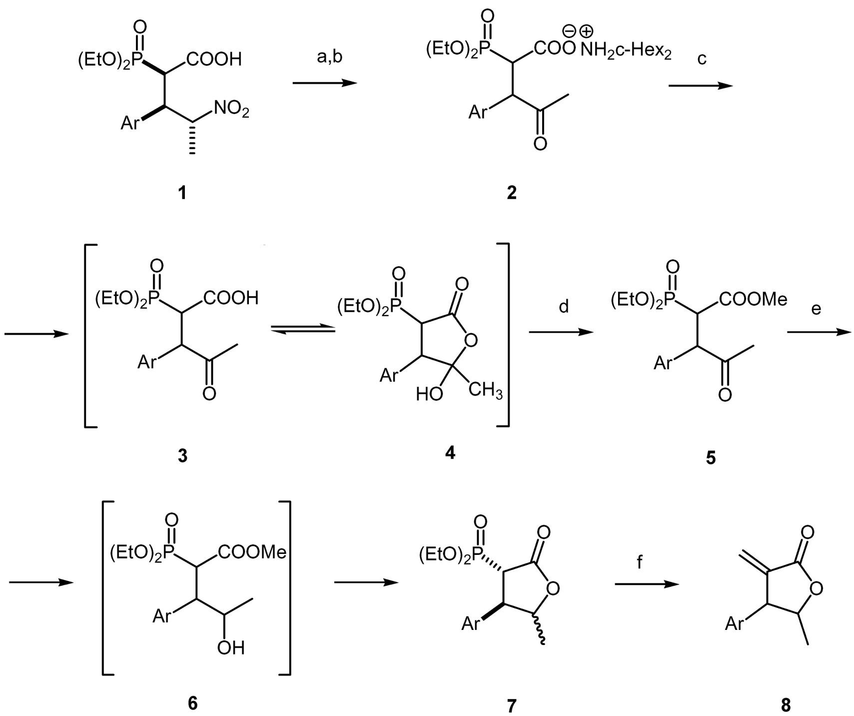
In the course of our earlier studies, we reported the synthesis of 3-aryl-2-diethoxyphosphoryl-4-nitroalkanoic acids **1** as well as their conversion into the corresponding 3-aryl-2-diethoxyphosphoryl-4-oxopentanoic acids **3** by means of a spontaneous Nef reaction.[47] The resulting acids were isolated as dicyclohexylammonium salts **2**. It became clear that alkanoates of this type are particularly well suited for the preparation of β,γ-disubstituted α-diethoxyphosphoryl-γ-lactones.

This article reports on an effective and original synthesis of a series of β,γ-disubstituted α-diethoxyphosphoryl-γ-lactones **7** from the salts **2**. Transformation of α-diethoxyphosphoryl-γ-lactones **7** into the corresponding α-methylene-γ-lactones **8** is also described.

RESULTS AND DISCUSSION

Scheme 1 outlines the transformation of dicyclohexylammonium 3-aryl-2-diethoxyphosphoryl-4-oxopentanoates **2** into the corresponding α-methylene-γ-lactones **8**. The salts **2** were subjected to ion-exchange chromatography. It was found that the pure acids **3** could not be obtained by this method, most likely due to equilibrium with the corresponding γ-hydroxylactones **4**. Therefore, we decided to convert the mixtures of the products obtained directly to the esters **5**. The esterification was performed using methyl iodide in the presence of potassium carbonate and provided the corresponding esters **5** in high yields, each as a mixture of diasteroisomers in a ratio shown in Table I.

With the suitable substrates in hand, we turned our attention to their effective conversion into substituted α-methylene-γ-lactones **8**. The chemoselective reduction of the carbonyl group in the γ-oxoalkanoates **5** with potassium borohydride afforded the corresponding γ-hydroxyalkanoates **6**, which spontaneously lactonized to the corresponding α-diethoxyphosphoryl-γ-lactones **7**. The ^{31}P NMR spectra



SCHEME 1 *Reagents and conditions:* (a) H_2O, reflux; (b) $cHex_2NH$ (1.1 equiv), CH_2Cl_2, rt; (c) Dowex 50W, acetone/water, (d) K_2CO_3 (2.1 equiv), CH_3I (4 equiv), acetone, rt, 4 days; (e) KBH_4 (1.5 equiv), MeOH, O°C, 65 minutes; (f) *t*-BuOK (1.2 equiv), THF, rt, 0.5 h.; then $(HCHO)_n$ (5 equiv), THF, rt, 1 h.

TABLE I Methyl 4-Aryl-2-diethoxyphosphoryl-4-oxopentanoates 5a–e, 4-Aryl-3-diethoxyphosphoryl-5-methyldihydrofuran-2(3*H*)-ones 7a–e, and 4-Aryl-5-methyl-3-methylenedihydrofuran-2(3*H*)-ones 8a–e Prepared

Ar	4-Oxopentanoates **5**		α-Diethoxyphosphoryl-γ-lactones **7**		α-Methylene-γ-lactones **8**	
	Yield [%]	dr	Yield [%]	dr	Yield [%]	dr (*cis*:*trans*)
a 4-NO_2-C_6H_4-	90	1:0.09	76	0.51:1	72	0.51:1
b 4-Br-C_6H_4-	92	1:0.14	88	0.68:1	76	0.68:1
c 4-CH_3-C_6H_4-	81	1:0.52	85	0.87:1	61	0.87:1
d 4-CH_3O-C_6H_4-	87	1:0.40	77	0.94:1	71	0.94:1
e 3,4-$(OCH_2O)C_6H_3$-	92	1:0.42	78	0.95:1	66	0.95:1

of these compounds revealed the presence of two signals in a ratio shown in Table I. The mixtures of diastereomeric lactones could not be separated by column chromatography. The ^{1}H NMR data indicated that diastereomeric lactones **7** differed in relative configuration at the stereogenic centers C-4 and C-5. Unfortunately, the spectral data were insufficient to assign unequivocally the relative configuration of the stereogenic centers C-3 and C-4. The relative stereochemistry was assigned to be *trans* by analogy with the results of our earlier work.[40]

Then we focused our attention on the Horner—Wadsworth–Emmons olefination of formaldehyde with α-diethoxyphosphoryl-γ-lactones **7**. The reaction was performed in diethyl ether in the presence of potassium *tert*-butoxide as a base following our previously described procedure[42] and provided α-methylene-γ-lactones **8**, each as a mixture of two diastereoisomers. The mixtures of diastereomeric lactones were separated by column chromatography. The assignment of relative configuration to particular diastereoisomers was based on the analysis of the ^{1}H NMR spectra, by taking into account the shielding effect exerted by the aryl group and methyl group on the substituents at C-4 and C-5 located in the *cis* position. In general, the signals from the substituents (methyl group, C-4 and C-5 protons) *cis*-oriented to aryl or methyl group appeared at higher field with respect to those of *trans*-oriented substituents. It is worth noting that the ratios of diastereomeric α-methylene-γ-lactones **8** reflect the degree of diastereoselection which is attained in the reduction of oxoesters **5**.

In conclusion, we have succeeded in developing the simple and efficient synthesis of β,γ-disubstituted α-diethoxyphosphoryl-γ-lactones from easily available dicyclohexylammonium 3-aryl-2-diethoxyphosphoryl-4-oxopentanoates. Moreover, we have shown that the corresponding α-phosphono-γ-lactones can be utilized for the synthesis of biologically important α-methylene-γ-lactones. The protocol benefits from easily available starting materials, experimental simplicity, and high efficiency.

EXPERIMENTAL

NMR spectra were recorded with 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, using tetramethylsilane as an internal and 85% H_3PO_4 as an external standard. The number of protons at the carbon atoms was determined by DEPT experiments. IR spectra were measured with a Specord M80 (Zeiss) instrument. Elemental analyses were performed with a

Perkin-Elmer PE 2400 analyzer. Melting points were determined in open capillaries and are uncorrected. Dicyclohexylammonium 3-aryl-2-diethoxyphosphoryl-4-oxopentanoates **2a–e** were prepared according to the previously described procedure.[47]

Methyl 3-Aryl-2-(diethoxyphosphoryl)-4-oxopentanoates 5a–e: General Procedure

Ion-exchange chromatography of the salts **2** was performed on a glass column packed with Dowex 50W using H_2O/acetone (1:1) as eluent. The eluent was evaporated under reduced pressure, affording the crude acids **3** as viscous oils, which were subjected to the next step without any further purification. To a solution of a corresponding acid **3** (3 mmol) in acetone (15 mL), K_2CO_3 (869 mg, 6.3 mmol) and methyl iodide (1.704 g, 12 mmol) were added, and the resulting mixture was stoppered tightly and stirred at room temperature for 4 days. The reaction progress was occasionally monitored by ^{31}P NMR spectroscopy. After the acid **3** was completely reacted, the acetone was removed under reduced pressure, and water was added (10 mL). The water layer was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried over $MgSO_4$. Evaporation of the solvent under reduced pressure afforded a crude product, which was purified by column chromatography (eluent:ethyl acetate/hexane 2:1) or crystallized from diethyl ether.

Methyl 2-(Diethoxyphosphoryl)-3-(4-nitrophenyl)-4-oxopentanoate (5a)

(1.046 g, 90%), white solid. IR (CCl_4): $\nu = 1728, 1528, 1344, 1288, 1152, 1016\ cm^{-1}$. ^{31}P NMR ($CDCl_3$): $\delta = 20.0, 20.4$ (1 : 0.09); **(2*R**,3*S**)-5a**: ^{31}P NMR ($CDCl_3$): $\delta = 20.0$. ^{1}H NMR ($CDCl_3$): $\delta = 1.08$ (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3CH_2OP), 1.16 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3CH_2OP), 2.09 (s, 3H, CH_3CO), 3.68–4.03 (m, 3H, CH_3CH_2OP, CHP), 3.79 (d, $^5J_{PH} = 0.6$ Hz, 3H, CH_3OC, major), 4.05–4.25 (d, 2H, CH_3CH_2OP), 4.68 (dd, $^3J_{HH} = 11.7$ Hz, $^3J_{PH} = 7.7$ Hz, 1H, CHAr), 7.50 (d, $^3J_{HH} = 8.8$ Hz, 2H, arom-H), 8.22 (d, $^3J_{HH} = 8.8$ Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 15.7$ (d, $^3J_{PC} = 4.1$ Hz, CH_3CH_2OP), 15.8 (d, $^3J_{PC} = 5.4$ Hz, CH_3CH_2OP), 28.6 (CH_3CO), 47.9 (d, $^1J_{PC} = 131.5$ Hz, PCH), 52.6 (ArCH), 57.0 ($COOCH_3$), 62.4 (d, $^2J_{PC} = 6.5$ Hz, CH_3CH_2OP), 62.6 (d, $^2J_{PC} = 6.8$ Hz, CH_3CH_2OP), 123.7 (CH_{Ar}), 130.2 (CH_{Ar}), 141.7 (C_{Ar}), 147.5 (C_{Ar}), 168.6 (d, $^2J_{PC} = 5.1$ Hz, $COOCH_3$), 204.3 (d, $^3J_{PC} = 16.2$ Hz, CH_3CO). Anal. Calcd for $C_{16}H_{22}NO_8P$: C, 49.62; H, 5.73; N, 3.62. Found: C, 49.54; H, 5.67; N, 3.52%.

Methyl 3-(4-Bromophenyl)-2-(diethoxyphosphoryl)-4-oxopentanoate (5b)

(1.162 g, 92%), white solid. IR (CCl_4): $\nu =$ 1720, 1488, 1348, 1292, 1256, 1156, 1024 cm^{-1}. ^{31}P NMR ($CDCl_3$): $\delta =$ 20.9, 21.3 (1: 0.14). ^{1}H NMR ($CDCl_3$): $\delta =$ 1.08 (dt, $^3J_{HH} =$ 7.1 Hz, $^4J_{HP} =$ 0.5 Hz, 3H, CH_3CH$_2$OP, major), 1.15 (dt, $^3J_{HH} =$ 7.1 Hz, $^4J_{HP} =$ 0.6 Hz, 3H, CH_3CH$_2$OP, major), 1.30 (dt, $^3J_{HH} =$ 7.1 Hz, $^4J_{HP} =$ 0.6 Hz, 3H, CH_3CH$_2$OP, minor), 1.38 (dt, $^3J_{HH} =$ 7.1 Hz, $^4J_{HP} =$ 0.6 Hz, 3H, CH_3CH$_2$OP, minor), 2.05 (s, 3H, CH_3CO, major), 2.19 (s, 3H, CH_3CO, minor), 3.47 (d, $^5J_{PH} =$ 0.6 Hz, 3H, CH_3OC, minor), 3.63–4.01 (m, 3H, CH$_3$CH_2OP, CHP), 3.77 (d, $^5J_{PH} =$ 0.7 Hz, 3H, CH_3OC, major), 4.03–4.24 (d, 2H, CH$_3$CH_2OP), 4.43 (dd, $^3J_{HH} =$ 11.7 Hz, $^3J_{PH} =$ 10.1 Hz, 1H, CHAr, minor), 4.52 (dd, $^3J_{HH} =$ 11.8 Hz, $^3J_{PH} =$ 7.9 Hz, 1H, CHAr, major), 7.15 (d, $^3J_{HH} =$ 8.6 Hz, 2H, arom-H, minor), 7.18 (d, $^3J_{HH} =$ 8.5 Hz, 2H, arom-H, major), 7.43 (d, $^3J_{HH} =$ 8.6 Hz, 2H, arom-H, minor), 7.48 (d, $^3J_{HH} =$ 8.5 Hz, 2H, arom-H, major). ^{13}C NMR ($CDCl_3$): $\delta =$ 15.5 (d, $^3J_{PC} =$ 6.0 Hz,CH$_3$CH$_2$OP, major), 15.6 (d, $^3J_{PC} =$ 6.1 Hz,CH$_3$CH$_2$OP, major), 15.8 (d, $^3J_{PC} =$ 5.3 Hz,CH$_3$CH$_2$OP, minor), 28.0 (CH$_3$CO, major), 28.9 (CH$_3$CO, minor), 47.7 (d, $^1J_{PC} =$ 131.7 Hz, PCH, major), 47.8 (d, $^1J_{PC} =$ 127.0 Hz, PCH, minor), 51.8 (ArCH, minor), 52.2 (ArCH, major), 55.5 (d, $^4J_{PC} =$ 2.3 Hz, COOCH$_3$, minor), 56.6 (COOCH$_3$, major), 62.0 (d, $^2J_{PC} =$ 6.7 Hz, CH$_3$$CH_2$OP, major), 62.2 (d, $^2J_{PC} =$ 6.8 Hz, CH$_3$$CH_2$OP, major), 62.6 (d, $^2J_{PC} =$ 6.7 Hz, CH$_3$$CH_2$OP, minor), 62.7 (d, $^2J_{PC} =$ 6.7 Hz, CH$_3$$CH_2$OP, minor), 121.7 ($C_{Ar}$, minor), 121.8 ($C_{Ar}$, major), 129.9 ($CH_{Ar}$, minor), 130.7 ($CH_{Ar}$, major), 131.6 ($CH_{Ar}$), 133.2 ($C_{Ar}$, major), 133.9 (d, $^3J_{PC} =$ 16.2 Hz, C_{Ar}, minor), 167.0 (d, $^2J_{PC} =$ 5.3 Hz, COOCH$_3$, minor), 168.6 (d, $^2J_{PC} =$ 4.9 Hz, COOCH$_3$, major), 203.9 (CH$_3$$C$O, minor), 204.8 (d, $^3J_{PC} =$ 16.6 Hz, CH$_3$$C$O, major). Anal. Calcd. for $C_{16}H_{22}BrO_6P$: C, 45.62; H, 5.26. Found: C, 45.70; H, 5.33%.

Methyl 2-(Diethoxyphosphoryl)-3-(4-methylphenyl)-4-oxopentanoate (5c)

(866 mg, 81%), yellow oil. IR (CCl_4): $\nu =$ 1724, 1436, 1352, 1264, 1156, 1048 cm^{-1}. ^{31}P NMR ($CDCl_3$): $\delta =$ 21.0, 21.5 (1 : 0.52). ^{1}H NMR ($CDCl_3$): $\delta =$ 1.05 (dt, $^3J_{HH} =$ 7.0 Hz, $^4J_{HP} =$ 0.5 Hz, 3H, CH_3CH$_2$OP, major), 1.13 (dt, $^3J_{HH} =$ 7.0 Hz, $^4J_{HP} =$ 0.8 Hz, 3H, CH_3CH$_2$OP, major), 1.30 (dt, $^3J_{HH} =$ 7.0 Hz, $^4J_{HP} =$ 0.8 Hz, 3H, CH_3CH$_2$OP, minor), 1.38 (dt, $^3J_{HH} =$ 7.0 Hz, $^4J_{HP} =$ 0.5 Hz, 3H, CH_3CH$_2$OP, minor), 2.04 (s, 3H, CH_3CO, major), 2.17 (s, 3H, CH_3CO, minor), 2.30 (s, 3H, CH_3Ar, minor), 2.33 (s, 3H, CH_3Ar, major), 3.44 (d, $^5J_{PH} =$ 0.5 Hz, 3H, CH_3OC, minor), 3.58–3.98 (m, 3H, CH$_3$CH_2OP, CHP), 3.77 (d, $^5J_{PH} =$ 0.5 Hz, 3H, CH_3OC, major), 4.06–4.22 (d, 2H, CH$_3$CH_2OP), 4.43 (dd, $^3J_{HH} =$ 11.8 Hz, $^3J_{PH} =$ 10.2 Hz,

1H, C*H*Ar, minor), 4.51 (dd, $^3J_{HH}$ = 12.0 Hz, $^3J_{PH}$ = 8.2 Hz, 1H, C*H*Ar, major), 7.10–7.13 (m, 4H, arom-H, minor), 7.15–7.16 (m, 4H, arom-H, major). ^{13}C NMR ($CDCl_3$): δ = 15.5 (d, $^3J_{PC}$ = 6.1 Hz,$\mathit{C}H_3CH_2$OP, major), 15.6 (d, $^3J_{PC}$ = 6.4 Hz,$\mathit{C}H_3CH_2$OP, major), 15.8 (d, $^3J_{PC}$ = 5.7 Hz,$\mathit{C}H_3CH_2$OP, minor), 15.9 (d, $^3J_{PC}$ = 5.5 Hz,$\mathit{C}H_3CH_2$OP, minor), 20.6 ($\mathit{C}H_3$Ar), 27.8 ($\mathit{C}H_3$CO, major), 28.7 ($\mathit{C}H_3$CO, minor), 47.8 (d, $^1J_{PC}$ = 131.2 Hz, P*C*H, minor), 47.9 (d, $^1J_{PC}$ = 132.1 Hz, P*C*H, major), 51.6 (Ar*C*H, minor), 52.1 (Ar*C*H, major), 55.9 (d, $^4J_{PC}$ = 2.7 Hz, $COO\mathit{C}H_3$, minor), 56.9 ($COO\mathit{C}H_3$, major), 61.9 (d, $^2J_{PC}$ = 7.0 Hz, $CH_3\mathit{C}H_2$OP, major), 62.0 (d, $^2J_{PC}$ = 7.2 Hz, $CH_3\mathit{C}H_2$OP, major), 62.4 (d, $^2J_{PC}$ = 6.6 Hz, $CH_3\mathit{C}H_2$OP, minor), 62.6 (d, $^2J_{CP}$ = 6.5 Hz, $CH_3\mathit{C}H_2$OP, minor), 128.1 ($\mathit{C}H_{Ar}$, minor), 128.8 ($\mathit{C}H_{Ar}$, major), 129.2 ($\mathit{C}H_{Ar}$), 131.1 (C_{Ar}, major), 131.7 (d, $^3J_{PC}$ = 16.0 Hz, C_{Ar}, minor), 137.3 (C_{Ar}, minor), 137.5 (C_{Ar}, major), 167.3 (d, $^2J_{PC}$ = 5.2 Hz, $\mathit{C}OOCH_3$, minor), 169.0 (d, $^2J_{PC}$ = 4.8 Hz, $\mathit{C}OOCH_3$, major), 204.4 ($CH_3\mathit{C}O$, minor), 205.4 (d, $^3J_{PC}$ = 16.8 Hz, $CH_3\mathit{C}O$, major). Anal. Calcd. for $C_{17}H_{25}O_6P$: C, 57.30; H, 7.07. Found: C, 57.42; H, 7.12%.

Methyl 2-(Diethoxyphosphoryl)-3-(4-methoxyphenyl)-4-oxopentanoate (5d)

(972 mg, 87%), yellow oil. ^{31}P NMR ($CDCl_3$): δ = 21.4, 21.8 (1 : 0.40). ^{1}H NMR ($CDCl_3$): δ = 1.06 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.5 Hz, 3H, $C\mathit{H}_3CH_2$OP, major), 1.14 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.6 Hz, 3H, $C\mathit{H}_3CH_2$OP, major), 1.30 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.5 Hz, 3H, $C\mathit{H}_3CH_2$OP, minor), 1.38 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.6 Hz, 3H, $C\mathit{H}_3CH_2$OP, minor), 2.04 (s, 3H, $C\mathit{H}_3$CO, major), 2.17 (s, 3H, $C\mathit{H}_3$CO, minor), 3.45 (d, $^5J_{PH}$ = 0.6 Hz, 3H, $C\mathit{H}_3$OC, minor), 3.60–4.00 (m, 3H, $CH_3C\mathit{H}_2$OP, C*H*P), 3.77 (d, $^5J_{PH}$ = 0.7 Hz, 3H, $C\mathit{H}_3$OC, major), 3.79 (s, 3H, $C\mathit{H}_3$OAr), 4.03–4.22 (d, 2H, $CH_3C\mathit{H}_2$OP), 4.41 (dd, $^3J_{HH}$ = 10.3 Hz, $^3J_{PH}$ = 10.1 Hz, 1H, C*H*Ar, minor), 4.50 (dd, $^3J_{HH}$ = 11.7 Hz, $^3J_{PH}$ = 8.1 Hz, 1H, C*H*Ar, major), 6.82 (d, $^3J_{HH}$ = 8.9 Hz, 2H, arom-H, minor), 6.87 (d, $^3J_{HH}$ = 8.8 Hz, 2H, arom-H, major), 7.17 (d, $^3J_{HH}$ = 8.9 Hz, 2H, arom-H, minor), 7.20 (d, $^3J_{HH}$ = 8.8 Hz, 2H, arom-H, major). ^{13}C NMR ($CDCl_3$): δ = 15.7 (d, $^3J_{PC}$ = 6.2 Hz,$\mathit{C}H_3CH_2$OP, major), 16.0 (d, $^3J_{PC}$ = 5.6 Hz,$\mathit{C}H_3CH_2$OP, minor), 27.9 ($\mathit{C}H_3$CO, major), 28.8 ($\mathit{C}H_3$CO, minor), 47.9 (d, $^1J_{PC}$ = 125.9 Hz, P*C*H, minor), 48.0 (d, $^1J_{PC}$ = 132.2 Hz, P*C*H, major), 51.8 (Ar*C*H, minor), 52.2 (Ar*C*H, major), 54.8 ($\mathit{C}H_3$OAr, minor), 54.9 ($\mathit{C}H_3$OAr, major), 55.5 (d, $^4J_{PC}$ = 2.7 Hz, $COO\mathit{C}H_3$, minor), 56.5 ($COO\mathit{C}H_3$, major), 62.0 (d, $^2J_{PC}$ = 7.2 Hz, $CH_3\mathit{C}H_2$OP, major), 62.1 (d, $^2J_{PC}$ = 7.4 Hz, $CH_3\mathit{C}H_2$OP, major), 62.5 (d, $^2J_{PC}$ = 6.6 Hz, $CH_3\mathit{C}H_2$OP, minor), 62.7 (d, $^2J_{PC}$ = 6.5 Hz, $CH_3\mathit{C}H_2$OP, minor), 113.9 ($\mathit{C}H_{Ar}$, minor), 114.0 ($\mathit{C}H_{Ar}$, major), 126.0 (C_{Ar}, major), 126.6 (d, $^3J_{PC}$ = 16.2 Hz, C_{Ar},

minor), 129.4 (CH$_{Ar}$, minor), 130.1 (CH$_{Ar}$, major), 159.0 (C_{Ar}, minor), 159.2 (C_{Ar}, major), 167.4 (d, $^2J_{PC}$ = 5.1 Hz, COOCH$_3$, minor), 169.1 (d, $^2J_{PC}$ = 4.9 Hz, COOCH$_3$, major), 204.5 (CH$_3C$O, minor), 205.6 (d, $^3J_{PC}$ = 16.8 Hz, CH$_3C$O, major). Anal. Calcd. for $C_{17}H_{25}O_7P$: C, 54.84; H, 6.77. Found: C, 54.71; H, 6.63%.

Methyl 2-(Diethoxyphosphoryl)-3-(3,4-methylenedioxyphenyl)-4-oxopentanoate (5e)

(1.066 g, 92%), yellow oil. IR (CCl$_4$): $\nu = 1736, 1488, 1440, 1352, 1248, 1160, 1040$ cm^{-1}. ^{31}P NMR (CDCl$_3$): δ = 20.9, 21.3 (1 : 0.42). ^{1}H NMR (CDCl$_3$): δ = 1.12 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.5 Hz, 3H, CH_3CH$_2$OP, major), 1.18 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.6 Hz, 3H, CH_3CH$_2$OP, major), 1.30 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.6 Hz, 3H, CH_3CH$_2$OP, minor), 1.38 (dt, $^3J_{HH}$ = 7.1 Hz, $^4J_{HP}$ = 0.6 Hz, 3H, CH_3CH$_2$OP, minor), 2.06 (s, 3H, CH_3CO, major), 2.19 (s, 3H, CH_3CO, minor), 3.50 (d, $^5J_{PH}$ = 0.6 Hz, 3H, CH_3OC, minor), 3.65–4.03 (m, 3H, CH$_3$CH_2OP, CHP), 3.77 (d, $^5J_{PH}$ = 0.7 Hz, 3H, CH_3OC, major), 4.06–4.23 (d, 2H, CH$_3$CH_2OP), 4.37 (dd, $^3J_{HH}$ = 11.8 Hz, $^3J_{PH}$ = 10.2 Hz, 1H, CHAr, minor), 4.46 (dd, $^3J_{HH}$ = 11.7 Hz, $^3J_{PH}$ = 8.1 Hz, 1H, CHAr, major), 5.94 (s, 2H, CH_2O$_2$Ar, minor), 5.95 (s, 2H, CH_2O$_2$Ar, major), 6.72–6.75 (m, 2H, arom-H), 6.77–6.79 (m, 1H, CH_{Ar}). ^{13}C NMR (CDCl$_3$): δ = 15.7 (d, $^3J_{PC}$ = 6.4 Hz,CH$_3$CH$_2$OP, major), 15.9 (d, $^3J_{PC}$ = 5.3 Hz,CH$_3$CH$_2$OP, minor), 27.8 (CH$_3$CO, major), 28.7 (CH$_3$CO, minor), 47.9 (d, $^1J_{PC}$ = 131.2 Hz, PCH), 51.8 (ArCH, minor), 52.3 (ArCH, major), 55.8 (COOCH$_3$, minor), 56.8 (COOCH$_3$, major), 62.1 (d, $^2J_{PC}$ = 7.3 Hz, CH$_3C$H$_2$OP, major), 62.2 (d, $^2J_{PC}$ = 8.2 Hz, CH$_3C$H$_2$OP, major), 62.6 (d, $^2J_{PC}$ = 6.6 Hz, CH$_3C$H$_2$OP, minor), 62.8 (d, $^2J_{PC}$ = 6.6 Hz, CH$_3C$H$_2$OP, minor), 100.9 (CH_2O$_2$Ar), 108.2 (CH$_{Ar}$, minor), 108.2 (CH$_{Ar}$), 108.9 (CH$_{Ar}$, major), 122.0 (CH$_{Ar}$, minor), 122.7 (CH$_{Ar}$, major), 127.6 (C_{Ar}, major), 128.2 (d, $^3J_{PC}$ = 16.5 Hz, C_{Ar}, minor), 147.1 (C_{Ar}, minor), 147.2 (C_{Ar}, major), 147.7 (C_{Ar}), 167.3 (d, $^2J_{PC}$ = 5.1 Hz, COOCH$_3$, minor), 169.0 (d, $^2J_{PC}$ = 4.7 Hz, COOCH$_3$, major), 204.4 (CH$_3C$O, minor), 205.4 (d, $^3J_{PC}$ = 16.8 Hz, CH$_3C$O, major). Anal. Calcd. for $C_{17}H_{23}O_8P$: C, 52.85; H, 6.00. Found: C, 52.92; H, 6.07%.

4-Aryl-3-diethoxyphosphoryl-5-methyldihydrofuran-2(3*H*)-ones (7a–e): General Procedure

To a stirred solution of 4-oxopentanoate **5** (2 mmol) in methanol (10 mL), potassium borohydride (168 mg, 3 mmol) was added in portions at 0°C. Stirring was continued for 65 min, and the reaction mixture was acidified to pH 1.5 with concentrated HCl. Next, water (10 mL) was added, and methanol was evaporated under reduced pressure. The residue was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic layers were dried over $MgSO_4$, and the solvent was evaporated under reduced pressure to afford a crude product, which was purified by column chromatography (eluent:$CHCl_3$/acetone 98:2).

3-Diethoxyphosphoryl-5-methyl-4-(4-nitrophenyl)dihydrofuran-2(3H)-one (7a)

(543 mg, 76%), pale yellow oil. IR (CCl_4): ν = 1778, 1382, 1262, 1024 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 18.7, 19.1 (0.51 : 1). ^{1}H NMR ($CDCl_3$): δ = 1.02 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3CH, minor), 1.13 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3CH_2OP, major), 1.28 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3CH_2OP, major), 1.31 (t, $^3J_{HH}$ = 7.1 Hz, 3H, minor), 1.37 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3CH_2OP, minor), 1.47 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3CH, major), 3.31 (dd, $^3J_{HH}$ = 3.6 Hz, $^3J_{PH}$ = 24.6 Hz, 1H, CHP, minor), 3.36 (dd, $^3J_{HH}$ = 10.8 Hz, $^3J_{PH}$ = 23.3 Hz, 1H, CHP, major), 3.48–3.76 (m, 1H, CHAr), 3.87–4.39 (m, 4H, CH_3CH_2OP), 4.54 (dq, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, OCH, major), 5.18 (dq, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, OCH, minor), 7.47–7.59 (m, 2H, arom-H), 8.16–8.27 (m, 2H, arom-H). ^{13}C NMR ($CDCl_3$): δ = 15.7 (d, $^3J_{PC}$ = 6.4 Hz,CH_3CH_2OP, minor), 15.8 (d, $^3J_{PC}$ = 6.0 Hz,CH_3CH_2OP, major), 16.3 (CH_3CH, minor), 18.4 (CH_3CH, major), 46.5 (d, $^1J_{PC}$ = 138.1 Hz, PCH, minor), 47.0 (ArCH, minor), 47.3 (d, $^1J_{PC}$ = 150.7 Hz, PCH, major), 51.5 (d, $^2J_{PC}$ = 1.4 Hz, ArCH, major), 62.3 (d, $^2J_{PC}$ = 6.8 Hz, CH_3CH_2OP, major), 62.9 (d, $^2J_{PC}$ = 6.6 Hz, CH_3CH_2OP, minor), 63.4 (d, $^2J_{PC}$ = 6.5 Hz, CH_3CH_2OP, major), 63.7 (d, $^2J_{PC}$ = 6.8 Hz, CH_3CH_2OP, minor), 78.4 (d, $^3J_{PC}$ = 4.6 Hz, OCH, minor), 81.5 (d, $^3J_{PC}$ = 12.9 Hz, OCH, major), 123.6 (CH_{Ar}, minor), 123.7 (CH_{Ar}, major), 128.7 (CH_{Ar}, major), 128.8 (CH_{Ar}, minor), 144.4 (C_{Ar}, minor), 144.6 (C_{Ar}, major), 146.7 (C_{Ar}, minor), 147.2 (C_{Ar}, major), 169.7 (COO, major), 170.6 (d, $^2J_{PC}$ = 3.2 Hz, COO, minor). Anal. Calcd. for $C_{15}H_{20}NO_7P$: C, 50.42; H, 5.64; N, 3.92. Found: C, 50.33; H, 5.71; N, 3.99%.

4-(4-Bromophenyl)-3-diethoxyphosphoryl-5-methyldihydrofuran-2(3H)-one (7b)

(688 mg, 88%), colorless oil. IR (CCl_4): ν = 1770, 1508, 1168, 1024 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 19.2, 19.5 (0.68 : 1). ^{1}H NMR ($CDCl_3$): δ = 1.01 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3CH, minor), 1.13 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3CH_2OP, major), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3CH_2OP, major), 1.31 (t, $^3J_{HH}$ = 7.0 Hz, 3H, minor), 1.36 (t, $^3J_{HH}$ = 7.0 Hz, 3H, CH_3CH_2OP, minor), 1.43 (d, $^3J_{HH}$ = 6.1 Hz, 3H, CH_3CH, major), 3.25 (dd, $^3J_{HH}$ = 3.4 Hz, $^3J_{PH}$ = 24.5 Hz, 1H, CHP, minor), 3.28 (dd, $^3J_{HH}$ = 10.8 Hz, $^3J_{PH}$ = 23.2 Hz, 1H, CHP, major), 3.44–3.59 (m, 1H, CHAr), 3.87–4.31 (m, 4H, CH_3CH_2OP), 4.46 (dq, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, OCH, major),

5.13 (dq, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, OC*H*, minor), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 2H, arom-H, minor), 7.14 (d, $^3J_{HH}$ = 8.5 Hz, 2H, arom-H, major), 7.48 (d, $^3J_{HH}$ = 8.4 Hz, 2H, arom-H, minor), 7.51 (d, $^3J_{HH}$ = 8.5 Hz, 2H, arom-H, major). ^{13}C NMR ($CDCl_3$): δ = 15.8 (d, $^3J_{PC}$ = 6.3 Hz,*C*H_3CH_2OP, minor), 16.0 (d, $^3J_{PC}$ = 5.7 Hz,*C*H_3CH_2OP, major), 16.5 (*C*H_3CH, minor), 18.6 (*C*H_3CH, major), 47.1 (Ar*C*H, minor), 47.5 (d, $^1J_{PC}$ = 149.6 Hz, P*C*H, major), 47.5 (d, $^1J_{PC}$ = 136.0 Hz, P*C*H, minor), 51.3 (d, $^2J_{PC}$ = 1.0 Hz, Ar*C*H, major), 61.3 (d, $^2J_{PC}$ = 6.7 Hz, CH_3*C*H_2OP, major), 62.9 (d, $^2J_{PC}$ = 6.8 Hz, CH_3*C*H_2OP, minor), 63.4 (d, $^2J_{PC}$ = 6.1 Hz, CH_3*C*H_2OP, major), 63.7 (d, $^2J_{PC}$ = 6.8 Hz, CH_3*C*H_2OP, minor), 79.0 (d, $^3J_{PC}$ = 3.5 Hz, O*C*H, minor), 82.2 (d, $^3J_{PC}$ = 12.9 Hz, O*C*H, major), 121.6 (C_{Ar}, major), 121.7 (C_{Ar}, minor), 129.2 (*C*H_{Ar}, major), 129.3 (*C*H_{Ar}, minor), 131.8 (*C*H_{Ar}, minor), 131.9 (*C*H_{Ar}, major), 136.5 (C_{Ar}, major), 136.6 (C_{Ar}, minor), 170.1 (d, $^2J_{PC}$ = 4.0 Hz, *C*OO, major), 171.2 (d, $^2J_{PC}$ = 3.6 Hz, *C*OO, minor). Anal. Calcd. for $C_{15}H_{20}BrO_5P$: C, 46.05; H, 5.15. Found: C, 46.14; H, 5.22%.

3-Diethoxyphosphoryl-5-methyl-4-(4-methylphenyl)dihydrofuran-2(3H)-one (7c)

(554 mg, 85%), colorless oil. IR (CCl_4): ν = 1772, 1388, 1256, 1028 cm^{-1}. ^{31}P NMR ($CDCl_3$): δ = 19.7, 19.9 (0.87 : 1). ^{1}H NMR ($CDCl_3$): δ = 1.00 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *C*H_3CH, minor), 1.11 (t, $^3J_{HH}$ = 7.1 Hz, 3H, C*H_3*CH_2OP, major), 1.24 (t, $^3J_{HH}$ = 7.0 Hz, 3H, C*H_3*CH_2OP, major), 1.31 (t, $^3J_{HH}$ = 7.0 Hz, 3H, minor), 1.36 (t, $^3J_{HH}$ = 7.0 Hz, 3H, C*H_3*CH_2OP, minor), 1.43 (d, $^3J_{HH}$ = 6.1 Hz, 3H, *C*H_3CH, major), 2.34 (s, 3H, CH_3Ar) 3.29 (dd, $^3J_{HH}$ = 3.0 Hz, $^3J_{PH}$ = 24.6 Hz, 1H, C*H*P, minor), 3.32 (dd, $^3J_{HH}$ = 10.8 Hz, $^3J_{PH}$ = 22.9 Hz, 1H, C*H*P, major), 3.43–3.63 (m, 1H, C*H*Ar), 3.68–4.30 (m, 4H, CH_3C*H_2*OP), 4.48 (dq, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.3 Hz, 1H, OC*H*, major), 5.13 (dq, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH}$ = 6.5 Hz, 1H, OC*H*, minor), 6.98–7.16 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$): δ = 15.6 (d, $^3J_{PC}$ = 6.4 Hz,*C*H_3CH_2OP, minor), 15.8 (d, $^3J_{PC}$ = 6.4 Hz,*C*H_3CH_2OP, major), 16.3 (*C*H_3CH, minor), 18.4 (*C*H_3CH, major), 20.6 (CH_3Ar), 47.0 (Ar*C*H, minor), 47.4 (d, $^1J_{PC}$ = 149.2 Hz, P*C*H, major), 47.7 (d, $^1J_{PC}$ = 135.3 Hz, P*C*H, minor), 51.3 (d, $^2J_{PC}$ = 1.1 Hz, Ar*C*H, major), 62.0 (d, $^2J_{PC}$ = 6.8 Hz, CH_3*C*H_2OP, major), 62.6 (d, $^2J_{PC}$ = 6.8 Hz, CH_3*C*H_2OP, minor), 63.1 (d, $^2J_{PC}$ = 6.2 Hz, CH_3*C*H_2OP, major), 63.3 (d, $^2J_{PC}$ = 6.7 Hz, CH_3*C*H_2OP, minor), 79.3 (d, $^3J_{PC}$ = 3.6 Hz, O*C*H, minor), 82.2 (d, $^3J_{PC}$ = 13.2 Hz, O*C*H, major), 127.2 (*C*H_{Ar}, major), 127.3 (*C*H_{Ar}, minor), 129.1 (*C*H_{Ar}, major), 129.2 (*C*H_{Ar}, minor), 134.1 (C_{Ar}, major), 134.4 (C_{Ar}, minor), 137.0 (C_{Ar}, minor), 137.2 (C_{Ar}, major), 170.2 (*C*OO, major), 171.4 (d, $^2J_{PC}$ = 3.7 Hz, *C*OO, minor). Anal. Calcd. for $C_{16}H_{23}O_5P$: C, 58.89; H, 7.10. Found: C, 58.76; H, 7.08%.

3-Diethoxyphosphoryl-4-(4-methoxyphenyl)-5-methyldihydrofuran-2(3H)-one (7d)

(527 mg, 77%), colorless oil. IR (CCl_4): $\nu = 1768, 1380, 1260, 1028$ cm^{-1}. ^{31}P NMR ($CDCl_3$): $\delta = 19.7, 19.9$ (0.86 : 1). ^{1}H NMR ($CDCl_3$): $\delta =$ 1.00 (d, $^3J_{HH} = 6.5$ Hz, 3H, CH_3CH, minor), 1.11 (dt, $^3J_{HH} = 7.1$ Hz, $^4J_{HH} = 0.5$ Hz, 3H, CH_3CH$_2$OP, major), 1.25 (dt, $^3J_{HH} = 7.1$ Hz, $^4J_{HH} =$ 0.5 Hz, 3H, CH_3CH$_2$OP, major), 1.31 (dt, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 0.5$ Hz, 3H, minor), 1.36 (dt, $^3J_{HH} = 7.0$ Hz, $^4J_{HH} = 0.5$ Hz, 3H, CH_3CH$_2$OP, minor), 1.42 (d, $^3J_{HH} = 6.1$ Hz, 3H, CH$_3$CH, major), 3.27 (dd, $^3J_{HH} =$ 3.2 Hz, $^3J_{PH} = 24.5$ Hz, 1H, CHP, minor), 3.27 (dd, $^3J_{HH} = 10.9$ Hz, $^3J_{PH} = 23.1$ Hz, 1H, CHP, major), 3.42–3.58 (m, 1H, CHAr), 3.75–4.30 (m, 4H, CH$_3$CH_2OP), 3.80 (s, 3H, CH$_3$OAr, minor), 3.81 (s, 3H, CH$_3$OAr, major), 4.46 (dq, $^3J_{HH} = 8.3$ Hz, $^3J_{HH} = 6.1$ Hz, 1H, OCH, major), 5.12 (dq, $^3J_{HH} = 6.5$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, OCH, minor), 6.87 (d, $^3J_{HH} =$ 8.7 Hz, arom-H, 2H, minor), 6.89 (d, $^3J_{HH} = 8.7$ Hz, 2H, arom-H, major), 7.03 (d, $^3J_{HH} = 8.7$ Hz, arom-H, 2H, minor), 7.18 (d, $^3J_{HH} = 8.7$ Hz, 2H, arom-H, major). ^{13}C NMR ($CDCl_3$): $\delta = 15.7$ (d, $^3J_{PC} = 6.4$ Hz,CH$_3$CH$_2$OP, minor), 15.9 (d, $^3J_{PC} = 5.9$ Hz,CH$_3$CH$_2$OP, major), 16.4 (CH$_3$CH, minor), 18.4 (CH$_3$CH, major), 46.7 (ArCH, minor), 47.5 (d, $^1J_{PC} = 149.6$ Hz, PCH, major), 47.8 (d, $^1J_{PC} = 136.0$ Hz, PCH, minor), 51.0 (d, $^2J_{PC} = 2.0$ Hz, ArCH, major), 54.9 (CH$_3$OAr, minor), 54.8 (CH$_3$OAr, major), 62.1 (d, $^2J_{PC} = 6.7$ Hz, CH$_3$$CH_2$OP, major), 62.7 (d, $^2J_{PC} = 6.8$ Hz, CH$_3$$CH_2$OP, minor), 63.1 (d, $^2J_{PC} = 6.4$ Hz, CH$_3$$CH_2$OP, major), 63.4 (d, $^2J_{PC} = 6.7$ Hz, CH$_3$$CH_2$OP, minor), 79.5 (d, $^3J_{PC} = 3.8$ Hz, OCH, minor), 82.3 (d, $^3J_{PC} = 13.4$ Hz, OCH, major), 113.9 (CH$_{Ar}$, major), 114.0 (CH$_{Ar}$, minor), 128.4 (CH$_{Ar}$, major), 128.5 (CH$_{Ar}$, minor), 129.0 (C_{Ar}, major), 129.4 (C_{Ar}, minor), 159.0 (C_{Ar}, major), 158.9 (C_{Ar}, minor), 170.3 (COO, major), 171.5 (d, $^2J_{PC} = 4.0$ Hz, COO, minor). Anal. Calcd. for $C_{16}H_{23}O_6P$: C, 56.14; H, 6.77. Found: C, 56.27; H, 6.85%.

3-Diethoxyphosphoryl-5-methyl-4-(3,4-methylenedioxyphenyl)dihydrofuran-2(3H)-one (7e)

(1.21 g, 56%), pale-yellow oil. IR (CCl_4): $\nu = 1772, 1512, 1376, 1258$, 1020 cm^{-1}. ^{31}P NMR ($CDCl_3$): $\delta = 19.5, 19.8$ (0.95 : 1). ^{1}H NMR ($CDCl_3$): $\delta = 1.05$ (d, $^3J_{HH} = 6.5$ Hz, 3H, CH$_3$CH, minor), 1.16 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3CH$_2$OP, major), 1.27 (t, $^3J_{HH} = 7.1$ Hz, 3H, CH_3CH$_2$OP, major), 1.32 (t, $^3J_{HH} = 7.0$ Hz, 3H, minor), 1.36 (t, $^3J_{HH} = 7.0$ Hz, 3H, CH_3CH$_2$OP, minor), 1.43 (d, $^3J_{HH} = 6.1$ Hz, 3H, CH$_3$CH, major), 3.25 (dd, $^3J_{HH} = 2.9$ Hz, $^3J_{PH} = 24.5$ Hz, 1H, CHP, minor), 3.27 (dd, $^3J_{HH} =$ 10.7 Hz, $^3J_{PH} = 8.2$ Hz, 1H, CHP, major), 3.39–3.61 (m, 1H, CHAr), 3.76–4.32 (m, 4H, CH$_3$CH_2OP), 4.45 (dq, $^3J_{HH} = 8.2$ Hz, $^3J_{HH} = 6.1$ Hz, 1H, OCH, major), 5.10 (dq, $^3J_{HH} = 6.5$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, OCH, minor), 5.97 (s, 2H, CH_2O_2Ar), 6.56–6.60 (m, 1H, CH_{Ar}), 6.74–6.81 (m, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 15.9$ (d, $^3J_{PC} = 6.4$ Hz,CH_3CH_2OP, minor), 16.1 (d, $^3J_{PC} = 6.1$ Hz,CH_3CH_2OP, major), 16.5 (CH_3CH, minor), 18.8 (CH_3CH, major), 47.4 (d, $^2J_{PC} = 1.4$ Hz, ArCH, minor), 47.8 (d, $^1J_{PC} = 149.2$ Hz, PCH, major), 48.2 (d, $^1J_{PC} = 134.9$ Hz, PCH, minor), 51.5 (d, $^2J_{PC} = 2.0$ Hz, ArCH, major), 62.4 (d, $^2J_{PC} = 6.7$ Hz, CH_3CH_2OP, major), 62.9 (d, $^2J_{PC} = 6.8$ Hz, CH_3CH_2OP, minor), 63.5 (d, $^2J_{PC} = 6.3$ Hz, CH_3CH_2OP, major), 63.7 (d, $^2J_{PC} = 6.7$ Hz, CH_3CH_2OP, minor), 79.6 (d, $^3J_{PC} = 3.3$ Hz, OCH, minor), 82.5 (d, $^3J_{PC} = 13.1$ Hz, OCH, major), 101.2 (CH_2O_2Ar), 107.4 (CH_{Ar}, major), 107.9 (CH_{Ar}, minor), 108.3 (CH_{Ar}, minor), 108.4 (CH_{Ar}, major), 121.0 (CH_{Ar}, minor), 121.1 (CH_{Ar}, major), 131.3 (C_{Ar}, major), 131.4 (C_{Ar}, minor), 147.1 (C_{Ar}, minor), 147.2 (C_{Ar}, major), 148.0 (C_{Ar}, minor), 148.1 (C_{Ar}, major), 170.3 (COO, major), 171.6 (d, $^2J_{PC} = 4.2$ Hz, COO, minor). Anal. Calcd. for $C_{16}H_{21}O_7P$: C, 53.93; H, 5.94. Found: C, 53.99; H, 6.01%.

4-Aryl-5-methyl-3-methylenedihydrofuran-2(3*H*)-ones (8a–e): General Procedure

To a stirred solution of the corresponding 4-aryl-3-diethoxyphosphoryl-5-methyl-dihydrofuran-2(3*H*)-one **7** (1 mmol) in diethyl ether (10 mL), potassium *tert*-butoxide (134 mg, 1.2 mmol) was added, and the resulting mixture was stirred at room temperature for 30 min. Then paraformaldehyde (150 mg, 5 mmol) was added in one portion. After 1 h, the reaction mixture was quenched with brine (10 mL), and the water layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried over $MgSO_4$ and evaporated. The crude product was purified by column chromatography (eluent:ethyl acetate/hexane 4:1). Separation of diastereoisomers was accomplished by column chromatography using ethyl acetate:hexane 1:4 as eluent.

*5-Methyl-3-methylene-4-(4-nitrophenyl)dihydrofuran-2(3*H*)-one (8a)*

(168 mg, 72%), **(4*R**, 5*S**)-8a**: yellow oil. IR (film): $\nu = 1778, 1258, 1160, 1020$ cm^{-1}. ^{1}H NMR ($CDCl_3$): $\delta = 1.51$ (d, $^3J_{HH} = 6.2$ Hz, 3H, CH_3), 3.88 (ddd, $^3J_{HH} = 7.5$ Hz, $^4J_{HH} = 3.3$ Hz, $^4J_{HH} = 2.9$ Hz, 1H, CH−4), 4.50 (dq, $^3J_{HH} = 7.5$ Hz, $^3J_{HH} = 6.2$ Hz, 1H, CH−5), 5.42 (d, $^4J_{HH} = 2.9$ Hz, 1H, $H_2C{=}C$), 6.43 (d, $^4J_{HH} = 3.3$ Hz, 1H, $H_2C{=}C$), 7.43 (d, $^3J_{HH} = 8.6$ Hz, 2H, arom-H), 8.26 (d, $^3J_{HH} = 8.6$ Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): 19.9 (CH_3), 53.7 (C4), 80.9 (C5), 124.2 (CH_{Ar}), 124.1 ($H_2C{=}C$), 129.2 (CH_{Ar}), 139.2 (C_{Ar}), 145.8 (C_{Ar}), 147.4 ($CH_2 = C$), 168.7 (C2). Anal. Calcd. for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75. Found: C, 61.72;

H, 4.65%. **(4*R**,5*R**)-8a**: yellow oil. IR (film): ν = 1774, 1254, 1164, 1028 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.02 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 4.50 (ddd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.7 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, C*H*−4), 4.98 (dq, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*−5), 5.65 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H_2C=C), 6.55 (d, $^4J_{HH}$ = 2.7 Hz, 1H, H_2C=C), 7.36 (d, $^3J_{HH}$ = 8.9 Hz, 2H, arom-H), 8.24 (d, $^3J_{HH}$ = 8.9 Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): δ = 17.9 (CH_3), 49.0 (*C*4), 76.8 (*C*5), 123.8 (CH_{Ar}), 123.0 (H_2C=C), 129.9 (CH_{Ar}), 137.8 (C_{Ar}), 144.9 (C_{Ar}), 147.3 (CH_2 = *C*), 169.3 (*C*2). Anal. Calcd. for $C_{12}H_{11}NO_4$: C, 61.80; H, 4.75. Found: C, 61.95; H, 4.83%.

4-(4-Bromophenyl)-5-methyl-3-methylenedihydrofuran-2(3H)-one (8b)

(203 mg, 76%). **(4*R**, 5*S**)-8b**: pale-yellow oil. IR (film): ν = 1780, 1250, 1160, 1024 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.47 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 3.68 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 3.3 Hz, $^4J_{HH}$ = 3.0 Hz, 1H, C*H*−4), 4.43 (dq, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, C*H*−5), 5.38 (d, $^4J_{HH}$ = 3.0 Hz, 1H, H_2C=C), 6.36 (d, $^4J_{HH}$ = 3.3 Hz, 1H, H_2C=C), 7.10 (d, $^3J_{HH}$ = 8.3 Hz, 2H, arom-H), 7.52 (d, $^3J_{HH}$ = 8.3 Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): δ = 19.7 (CH_3), 53.8 (*C*4), 81.4 (*C*5), 121.9 (C_{Ar}), 123.5 (H_2C=C), 130.0 (CH_{Ar}), 132.3 (CH_{Ar}), 139.9 (C_{Ar}), 137.3 (CH_2 = *C*), 169.2 (*C*2). Anal. Calcd. for $C_{12}H_{11}BrO_2$: C, 53.96; H, 4.15. Found: C, 53.83; H, 4.07%. **(4*R**,5*R**)-8b**: colorless oil. IR (film): ν = 1776, 1256, 1164, 1020 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.00 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 4.35 (ddd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 2.2 Hz, $^4J_{HH}$ = 2.5 Hz, 1H, C*H*−4), 4.92 (dq, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.8 Hz, 1H, C*H*−5), 5.61 (d, $^4J_{HH}$ = 2.2 Hz, 1H, H_2C=C), 6.48 (d, $^4J_{HH}$ = 2.5 Hz, 1H, H_2C=C), 7.04 (d, $^3J_{HH}$ = 8.2 Hz, 2H, arom-H), 7.50 (d, $^3J_{HH}$ = 8.2 Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): δ = 18.1 (CH_3), 49.0 (*C*4), 77.3 (*C*5), 121.7 (C_{Ar}), 124.7 (H_2C=C), 130.6 (CH_{Ar}), 131.9 (CH_{Ar}), 136.3 (C_{Ar}), 138.4 (CH_2 = *C*), 169.9 (*C*2). Anal. Calcd. for $C_{12}H_{11}BrO_2$: C, 53.96; H, 4.15. Found: C, 53.80; H, 4.04.

5-Methyl-3-methylene-4-(4-methylphenyl)dihydrofuran-2(3H)-one (8c)

(123 mg, 61%). **(4*R**, 5*S**)-8c**: colorless oil. IR (film): ν = 1764, 1280, 1224, 1160 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.46 (d, $^3J_{HH}$ = 6.2 Hz, 3H, CH_3), 2.36 (s, 3H, CH_3Ar), 3.68 (ddd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 3.5 Hz, $^4J_{HH}$ = 3.0 Hz, 1H, C*H*-4), 4.45 (dq, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 6.2 Hz, 1H, C*H*−5), 5.38 (d, $^4J_{HH}$ = 3.0 Hz, 1H, H_2C=C), 6.33 (d, $^4J_{HH}$ = 3.5 Hz, 1H, H_2C=C), 7.10 (d, $^3J_{HH}$ = 8.2 Hz, 2H, arom-H), 7.19 (d, $^3J_{HH}$ = 8.2 Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): δ = 19.7 (CH_3), 21.0 (CH_3Ar), 54.0

(*C*4), 81.8 (*C*5), 123.2 (H_2C=C), 128.1 (*C*H_{Ar}), 129.7 (*C*H_{Ar}), 135.2 (C_{Ar}), 137.6 (C_{Ar}), 140.5 (CH_2 = *C*), 169.7 (*C*2). Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.13; H, 6.85%. **(4*R**, 5*R**)-8c**: pale yellow oil. IR (film): $\nu = 1768, 1384, 1224, 1160, 1064\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 0.99$ (d, $^3J_{HH} = 6.5$ Hz, 3H, C*H_3*), 2.35 (s, 3H, C*H_3*Ar), 4.34 (ddd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 3.0$ Hz, $^4J_{HH} = 2.5$ Hz, 1H, C*H*-4), 4.90 (dq, $^3J_{HH} = 8.0$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, C*H*-5), 5.61 (d, $^4J_{HH} = 2.5$ Hz, 1H, *H_2*C=C), 6.46 (d, $^4J_{HH} = 3.0$ Hz, 1H, *H_2*C=C), 7.03 (d, $^3J_{HH} = 8.2$ Hz, 2H, arom-H), 7.16 (d, $^3J_{HH} = 8.2$ Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 18.1$ (*C*H_3), 21.0 (*C*H_3Ar), 49.2 (*C*4), 77.9 (*C*5), 124.3 (H_2C=C), 128.9 (*C*H_{Ar}), 129.4 (*C*H_{Ar}), 129.9 (C_{Ar}), 134.1 (C_{Ar}), 138.8 (CH_2 = *C*), 170.4 (*C*2). Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.33; H, 7.09%.

4-(4-Methoxyphenyl)-5-methyl-3-methylenedihydrofuran-2(3H)-one (8d)

(155 mg, 71%). **(4*R**, 5*S**)-8d**: colorless oil. IR (film): $\nu = 1768, 1512, 1252\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 1.46$ (d, $^3J_{HH} = 6.2$ Hz, 3H, C*H_3*), 3.66 (ddd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 3.4$ Hz, $^4J_{HH} = 3.0$ Hz, 1H, C*H*-4), 3.82 (s, 3H, C*H_3*OAr), 4.43 (dq, $^3J_{HH} = 8.0$ Hz, $^3J_{HH} = 6.2$ Hz, 1H, C*H*5), 5.38 (d, $^4J_{HH} = 3.0$ Hz, 1H, *H_2*C=C), 6.33 (d, $^4J_{HH} = 3.4$ Hz, 1H, *H_2*C=C), 6.91 (d, $^3J_{HH} = 8.8$ Hz, 2H, arom-H), 7.13 (d, $^3J_{HH} = 8.8$ Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 19.6$ (*C*H_3), 53.8 (*C*H_3OAr), 55.2 (*C*4), 81.2 (*C*5), 114.5 (*C*H_{Ar}), 123.0 (H_2*C* =C), 129.4 (*C*H_{Ar}), 130.1 (C_{Ar}), 140.7 (C_{Ar}), 159.2 (CH_2 = *C*), 169.7 (*C*2). Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.39; H, 6.32%. **(4*R**,5*R**)-8d**: colorless oil. IR (film): $\nu = 1764, 1512, 1256\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 0.99$ (d, $^3J_{HH} = 6.5$ Hz, 3H, C*H_3*), 3.82 (s, 3H, C*H_3*OAr), 4.33 (ddd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 3.0$ Hz, $^4J_{HH} = 2.8$ Hz, 1H, C*H*−4), 4.89 (dq, $^3J_{HH} = 8.0$ Hz, $^3J_{HH} = 6.5$ Hz, 1H, C*H*−5), 5.60 (d, $^4J_{HH} = 2.8$ Hz, 1H, *H_2*C=C), 6.46 (d, $^4J_{HH} = 3.0$ Hz, 1H, *H_2*C=C), 6.89 (d, $^3J_{HH} = 8.8$ Hz, 2H, arom-H), 7.07 (d, $^3J_{HH} = 8.8$ Hz, 2H, arom-H). ^{13}C NMR ($CDCl_3$): $\delta = 18.1$ (*C*H_3), 48.9 (*C*4), 55.2 (*C*H_3OAr), 78.0 (*C*5), 114.1 (*C*H_{Ar}), 124.2 (H_2*C* =C), 129.1 (C_{Ar}), 130.1 (*C*H_{Ar}), 138.9 (C_{Ar}), 159.0 (CH_2 = *C*), 170.4 (*C*2). Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.45; H, 6.38%.

5-Methyl-3-methylene-4-(3,4-methylenedioxyphenyl) dihydrofuran-2(3H)-one (8e)

(153 mg, 66%). **(4*R**, 5*S**)-8e**: pale yellow oil. IR (film): $\nu = 1772, 1516, 1278, 1250\ cm^{-1}$. ^1H NMR ($CDCl_3$): $\delta = 1.46$ (d, $^3J_{HH} = 6.0$ Hz, 3H, C*H_3*), 3.63 (ddd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 3.2$ Hz, $^4J_{HH} = 2.8$ Hz, 1H, C*H*-4), 4.40 (dq, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 6.0$ Hz, 1H, C*H*-5), 5.42

(d, $^4J_{HH} = 2.8$ Hz, 1H, H_2C=C), 5.98 (s, 2H, CH_2O$_2$), 6.35 (d, $^4J_{HH} = 3.2$ Hz, 1H, H_2C=C), 6.67 (s, 1H, CH_{Ar}), 6.68 (d, $^3J_{HH} = 7.8$ Hz, 1H, CH_{Ar}), 6.80 (d, $^3J_{HH} = 7.8$ Hz, 1H, CH_{Ar}). ^{13}C NMR (CDCl$_3$): $\delta = 19.6$ (CH$_3$), 53.8 (C4), 81.7 (C5), 101.2 (CH_2O$_2$), 108.3 (CH$_{Ar}$), 108.5 (CH$_{Ar}$), 121.9 (CH$_{Ar}$), 123.2 (H$_2C$ =C), 137.8 (C_{Ar}), 140.3 (C_{Ar}), 147.2 (CH$_2$ = C), 148.2 (C_{Ar}), 169.5 (C2). Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.12; H, 5.10%. **(4R^*, 5R^*)-8e**: pale yellow oil. IR (film): $\nu = 1768$, 1510, 2180, 1254 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.03 (d, $^3J_{HH} = 6.8$ Hz, 3H, CH_3), 4.31 (ddd, $^3J_{HH} = 7.8$ Hz, $^4J_{HH} = 2.5$ Hz, $^4J_{HH} = 2.2$ Hz, 1H, CH-4), 4.88 (dq, $^3J_{HH} = 7.8$ Hz, $^3J_{HH} = 6.8$ Hz, 1H, CH-5), 5.63 (d, $^4J_{HH} = 2.2$ Hz, 1H, H_2C=C), 5.98 (s, 2H, CH_2O$_2$), 6.47 (d, $^4J_{HH} = 2.5$ Hz, 1H, H_2C=C), 6.62 (s, 1H, CH_{Ar}), 6.63 (d, $^3J_{HH} = 8.2$ Hz, 1H, CH_{Ar}), 6.79 (d, $^3J_{HH} = 8.2$ Hz, 1H, CH_{Ar}). ^{13}C NMR (CDCl$_3$): $\delta = 18.0$ (CH$_3$), 49.2 (C4), 77.9 (C5), 101.2 (CH_2O$_2$), 108.4 (CH$_{Ar}$), 109.0 (CH$_{Ar}$), 122.1 (CH$_{Ar}$), 124.5 (H$_2$C=C), 130.8 (C_{Ar}), 138.7 (C_{Ar}), 147.1 (CH$_2$ = C), 147.9 (C_{Ar}), 170.2 (C2). Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.23; H, 5.21. Found: C, 67.37; H, 5.31%.

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