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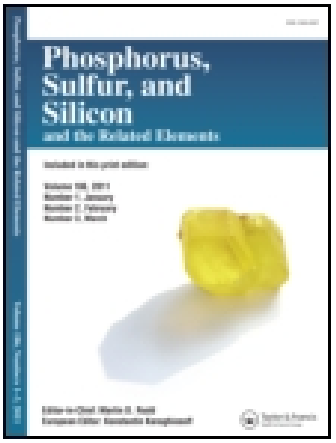

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A Facile Synthesis of Novel and Stable Phosphorus Ylides Containing 2-Aryl-1,3-Dioxane-4,6-Dione

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A FACILE SYNTHESIS OF NOVEL AND STABLE PHOSPHORUS YLIDES CONTAINING 2-ARYL-1,3-DIOXANE-4,6-DIONE

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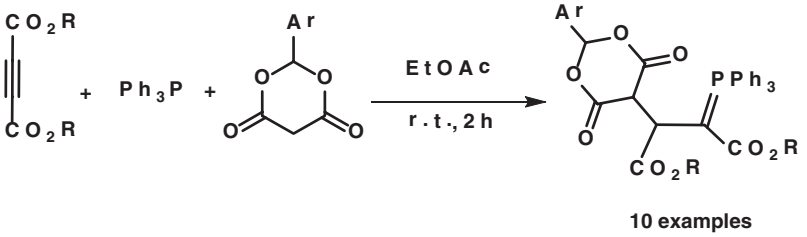
GRAPHICAL ABSTRACT



Abstract *The reaction between dialkyl acetylene dicarboxylate and 2-aryl-1,3-dioxane-4,6-dione derivatives in the presence of triphenylphosphine in ethyl acetate led to stable phosphorus ylides in good yields. These stabilized phosphorus ylides exist as a mixture of two geometrical isomers as a result of restricted rotation around the carbon–carbon partial double bond. The ^{1}H NMR variable temperature spectra for **3c** are studied and the results are reported.*

Keywords Triphenylphosphine; rotamers; stable phosphorus ylides; meldrum's acid

INTRODUCTION

In any organic synthesis plan, the formation of new carbon–carbon bonds poses a major challenge. Several methods have been developed for the synthesis of new compounds in which new carbon–carbon bond(s) is formed.[1] Among these, the application of phosphorus ylides is one of the most important routes for the formation of target organic compounds.[2] In recent years, interesting applications of phosphorus ylides for the preparations of industrial and pharmaceutical compounds have been reported.[3–16] Ylides are reactive intermediates that are usually prepared by the treatment of a phosphonium salt with a base, in which the phosphonium salts are obtained from triphenylphosphine and alkyl halide, and also Michael addition of phosphorus nucleophiles to activated olefins.

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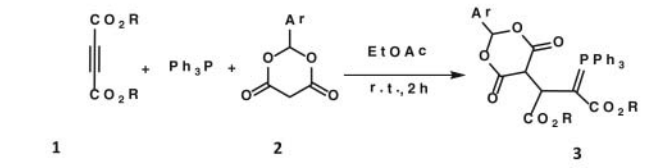
Recently, the use of phosphino-substituted iminium derivatives was published by Bertrand.[14] He reported that phosphino salts were prepared by the treatment of Alder's dimer or a chloro iminum salt with phosphines. Also, there are many studies on the reaction between trivalent phosphorus nucleophiles and acetylenic esters in the presence of a proton source.[15–18] In some cases, the ylide products are stable, but in others they cannot be isolated and act as intermediates on the pathway that produce the final isolated product.[12,18]

Our current studies are based on the application of Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) derivatives in multicomponent reactions.[19–22] Meldrum's acid and it's derivatives have attracted considerable attention as important intermediates in organic synthesis.[23–31]

Herein, we report an efficient synthetic route to congested phosphorus ylides **3** using triphenylphosphine, dialkyl acetylenedicarboxylates **1**, and 2-aryl-1,3-dioxane-4,6-dione **2** (Scheme 1).



1	R
a	Me
b	Et

2	Ar
a	
b	Cl
c	Me
d	MeO
e	F

3	R	Ar	%Yield
a	Me		81
b	Me	Cl	65
c	Me	Me	63
d	Me	MeO	71
e	Me	F	50
f	Et		72
g	Et	Cl	66
h	Et	Me	78
i	Et	MeO	77
j	Et	F	53

Scheme 1

RESULTS AND DISCUSSION

The reaction of dialkyl acetylenedicarboxylates **1** with 2-aryl-1,3-dioxane-4,6-dione derivatives **2** in the presence of triphenylphosphine proceeded smoothly at room temperature in ethyl acetate and was completed within a few hours. ^{1}H, ^{13}C NMR, and ^{31}P NMR spectra of the crude product clearly indicated the formation of ylides **3**. Any product other than **3** could not be detected by NMR spectroscopy.

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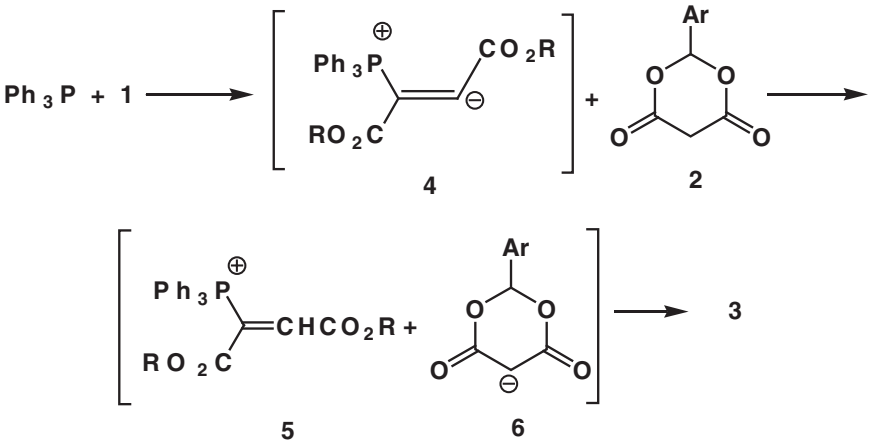
The structures of compounds **3a–j** were deduced from their elemental analyses and IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The most important absorption band in IR spectrum is the carbonyl group stretching, which appeared at 1633, 1695, and 1732 cm^{-1}.

The ^{1}H NMR spectrum of **3a** exhibited two signals at 3.29 and 3.60 ppm arising from the methoxy groups in the *Z*-isomer and two signals at 3.23 and 3.28 ppm for the methoxy group in the *E*-isomer. Signals for the methine protons between the two C=O appeared as two doublet of doublets at $\delta = 4.75$ ppm ($^{4}J_{PH} = 4.0$, $^{3}J_{HH} = 10.6$) and $\delta = 4.66$ ppm ($^{4}J_{PH} = 11.6$, $^{3}J_{HH} = 7.0$), for the *E*- and *Z*-isomers, respectively. Also, signals for the methine protons of P—C—CH appeared as doublet of doublets at $\delta = 5.67$ ppm ($^{3}J_{PH} = 11.0$, $^{3}J_{HH} = 11.0$) for the *E*-isomer and $\delta = 5.76$ ppm ($^{3}J_{PH} = 13.6$, $^{3}J_{HH} = 11.7$) for *Z*-isomer. Signals for Ph—CH appeared at 6.27 and 5.29 for the *E*- and *Z*-isomers, respectively. The aromatic protons (20 protons from four phenyl groups) appeared as a multiplet at $\delta = 7.25$–7.85. The ^{13}C NMR spectrum of **3a** showed 17 distinct resonances in agreement with the proposed structure. The ^{31}P NMR exhibited two signals at 23.2 and 23.4 ppm for the *E*- and *Z*-isomers, respectively.

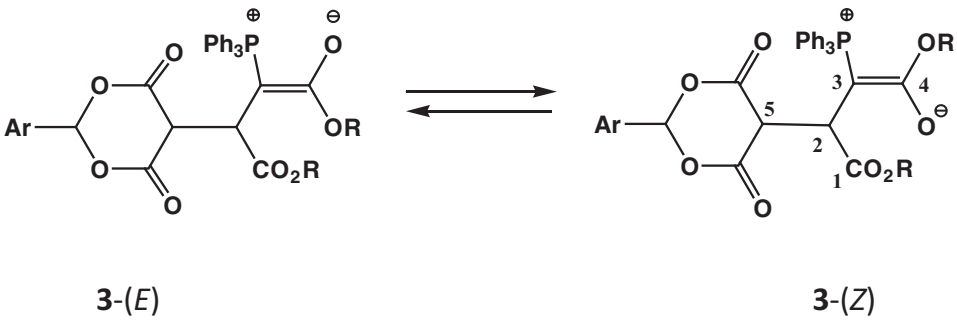
These ylides are interestingly stable in different boiling solvents (toluene, DMSO, and methanol) and they did not undergo any intramolecular reaction and the starting ylides were unchanged. However, they were destroyed under reflux in the presence of water and no isolable product was determined.

Even though we have not yet verified experimental evidence through kinetic studies for the mechanism of this reaction, in an earlier similar work, a reasonable mechanism was proposed.[8] On the basis of these reports, we can assume that initial addition of triphenylphosphine to the dialkyl acetylene dicarboxylate **1** can be formed zwitterions **4,** subsequently the protonation of intermediate **4** occurs by the C—H acid **2.** Then, Michael addition of anion **6** to the vinylphosphonium cation **5** generates phosphorane **3** (Scheme 2).



Scheme 2

The ^{1}H and ^{13}C NMR spectra of diastereomeric ylides **3a–j** were consistent with the presence of two geometric isomers. The ylide moiety of this compound is strongly conjugated to the adjacent carbonyl group and rotation around the partial double bond in the **3-(*E*)** and **3-(*Z*)** geometrical isomers is slow on the NMR time scale at ambient temperature (Scheme 3). The ^{1}H NMR spectrum of ylides shows individual signals for



Scheme 3

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two rotamers in the region of three CH substructure and OCH_2 (or OCH_3) fragment of the ester.

The methyl region of the ^{1}H NMR spectrum of **3c** in $CDCl_3$ at ambient temperature (25°C) exhibits two sharp singlets for the Methyl–Aryl groups of *E*- and *Z*-isomers. Increasing the temperature results in coalescence of the Me–Ar resonances. At 97 °C, a relatively broad singlet was observed for the Me–Ar group. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants for the Major (M) and Minor (m) rotamer isomers of compounds **3a–j** are given in Table 1.

Table 1 Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for H-2, H-5, CO_2R, OR, C-2, and C-3 in the major (M) and minor (m) rotamer isomers of compounds **3a–j**

		^{1}H NMR Data				^{13}C NMR Data		
Comp.	Isomer (%)	H-2 ($^3J_{PH}$)	H-5 ($^4J_{PH}$)	OR	CO_2R	C_2	C_3 ($^1J_{PH}$)	^{31}P
3a	M (55)	5.67 (11)	4.75 (4)	3.23	3.28	44.1	43.5 (91.3)	23.2
	m (45)	5.76 (13.6)	4.66 (7)	3.29	3.60	44.6	43.1 (52.1)	23.3
3b	M (55)	5.65 (11)	4.72 (4)	3.22	3.27	44.0	43.4 (92.8)	23.3
	m (45)	5.76 (13.6)	4.66 (7)	3.30	3.60	44.6	43.2 (52.8)	23.4
3c	M (55)	5.68 (11)	4.76 (4)	3.24	3.29	44.1	43.5 (92.0)	23.2
	m (45)	5.78 (13.6)	4.67 (7)	3.31	3.61	44.7	43.4 (52.1)	23.3
3d	M (54)	5.67 (11)	4.75 (4)	3.24	3.29	44.1	43.5 (91.3)	23.3
	m (46)	5.77 (13.6)	4.66 (7)	3.30	3.61	44.6	43.4 (52.1)	23.3
3e	M (58)	5.66 (11)	4.75 (4)	3.24	3.29	44.1	43.5 (91.3)	23.3
	m (42)	5.78 (13.6)	4.68 (7)	3.31	3.61	44.7	43.4 (52.1)	23.4
3f	M (64)	5.60 (11)	4.76 (3.4)	3.60	3.76	44.5	43.6 (135.8)	23.1
	m (36)	5.83 (13.6)	4.71 (6.8)	4.10	4.16	44.7	43.4 (60.4)	23.3
3g	M (64)	5.56 (11)	4.65 (3.4)	3.59	3.66	44.5	43.6 (138.8)	22.7
	m (36)	5.66 (13.6)	4.50 (6.8)	3.85	3.99	44.7	43.4 (60.4)	23.3
3h	M (67)	5.58 (11)	4.75 (3.4)	3.57	3.73	44.5	43.6 (135.8)	23.1
	m (33)	5.80 (13.6)	4.67 (6.8)	4.04	4.11	44.7	43.4 (60.4)	23.2
3i	M (64)	5.58 (11)	4.75 (3.4)	3.59	3.75	44.5	43.6 (135.8)	23.1
	m (36)	5.80 (13.6)	4.69 (6.8)	4.06	4.12	44.7	43.4 (60.4)	23.2
3j	M (67)	5.56 (11)	4.75 (3.4)	3.60	3.73	44.5	43.6 (135.8)	23.1
	m (33)	5.81 (13.6)	4.72 (6.8)	4.06	4.12	44.7	43.4 (60.4)	23.3

Table 2 Selected proton chemical shifts and activation parameters for **3c** in nitro benzene and **3h** in 1,2-dichlorobenzene

		Ar−CH_3					
Comp.	T (°C)	ppm		$\Delta\nu$ (Hz)	k (s^{-1})	T_c (K)	$\Delta G^{\neq}$
3c	22	2.30	2.33	9	20	368	19.5
	97	2.32					
3h	22	2.29	2.32	9	20	358	18.9
	85	2.34					

Although no extensive line-shape analysis for **3** was undertaken, the variable temperature spectra allowed to calculate the free barrier for the restricted C−C bond rotation in **3c**.

From the coalesence temperature of the methyl proton resonances and using the expression $k = {}^{\pi\Delta\vartheta}/\sqrt{2}$, we can calculate the first-order rate constant (k) for the dynamic NMR effect in **3c** is 20 s^{-1} at 368 K. Application of the absolute rate theory with a transmission coefficient of **1** gives a free energy of activation ($\Delta G^{\neq}$) of 19.5 ± 2 kJ mol^{-1} (Table 2), where all known sources of errors are estimated and included.

In conclusion, our procedure describes a smooth formation of new ylides of triphenylphosphine, dialkyl acetylenedicarboxylate, and 2-aryl-1,3-dioxane-4,6 dione. These ylides can be used as intermediate for synthesis of desired compounds.

EXPERIMENTAL

General Procedure for Preparation of 2a–e

A mixture was prepared by suspending a weighed quantity of the malonic acid (5.2 g, 0.05 mol) in three times its weight of 95% acetic anhydride [15.6 g (14.5 mL), 0.15 mol], adding concentrated sulfuric acid (0.05–0.1 mL), and allowing the mixture to stand overnight. The formed acetic acid and excess of anhydride were then removed in a water bath (below 40 °C) under reduced pressure. The aldehyde)0.05 mol(was then added to the residue and the mixture cooled with water. The mixture solidified after the addition of the aldehyde. The product was filtered.

2-phenyl-1,3-dioxane-4,6-dione (2a). White powder, mp 145 °C. FT-IR (KBr) (υ_{max}, cm^{-1}): 1805, 1764 (C=O). Anal. Calcd for $C_{10}H_8O_4$ (192.17); C, 62.5; H, 4.20%; Found: C, 62.50; H, 4.13%. ^{1}H NMR (300.1 MHz, acetone-d_6): δ 3.63 and 4.49 (2H, 2d, $^2J_{HH}$ = 18 Hz, CH_2), 7.20 (1H, s, CH), 7.50–7.65 (5H, m, C_6H_5). ^{13}C NMR (75.5 MHz, acetone-d_6): δ 39.9 (CH_2), 98.5 (CH), 127.5 (C_{ortho} of C_6H_5), 129.6 (C_{para} of C_6H_5), 131.5 (C_{meta} of C_6H_5), 134.2 (C_{ipso}), 165.1 (2C=O).

2-(4-Chlorophenyl)-1,3-dioxane-4,6-dione (2b). White powder, mp 139 °C. FT-IR (KBr) (υ_{max}, cm^{-1}): 1807, 1765 (C=O). Anal. Calcd for $C_{10}H_7ClO_4$)226.61); C, 53.0; H, 3.11%; Found: C, 53.20; H, 2.94%. ^{1}H NMR (300.1 MHz, $CDCl_3$) :δ 3.68 and 3.84 (2H, d, $^2J_{HH}$ = 18 Hz, CH_2), 6.76 (1H, s, CH), 7.46 and 7.51 (4H, 2d, $^3J_{HH}$ = 8.7 Hz, Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 39.0 (CH_2), 97.2 (CH), 127.8 (C_{ortho} of C_6H_4), 129.3 (C_{meta} of C_6H_4), 131.5 (C−Cl), 134.2 (C_{ipso}), 162.7 (2C=O).

2-(4-methylphenyl)-1,3-dioxane-4,6-dione (2c). White powder, mp 106 °C. FT-IR)KBr) (υ_{max}, cm^{-1}): 1808, 1765 (C=O). Anal. Calcd for $C_{11}H_{10}O_4$)206.19); C,

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64.08; H, 4.69%; Found: C, 63.90; H, 4.56%. ^{1}H NMR)300.1 MHz, $CDCl_3$): δ 2.40)3H, s, CH_3(, 3.62 and 3.81)2H, 2d, $^2J_{HH}$ = 18 Hz, CH_2(, 6.76)1H, s, CH(, 7.27 and 7.42 (4H, 2d, $^3J_{HH}$ = 8.4 Hz, Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.4)CH_3), 39.0)CH_2(, 98.1)CH), 126.2) C_{ortho} of C_6H_4 (129.2) C_{meta} of C_6H_4), 129.7)C−CH_3(, 141.3)C_{ipso}), 163.3)2 C=O).

2-(4-methoxyphenyl)-1,3-dioxane-4,6-dione (2d). Pink powder, mp 134 °C. FT-IR)KBr) (υ_{max}, cm^{-1}): 1806, 1766 (C=O). Anal. Calcd for $C_{11}H_{10}O_5$ (222.19); C, 59.46; H, 4.54%; Found: C, 59.49; H, 4.35%. ^{1}H NMR)300.1 MHz, acetone-d_6): δ 3.59 and 4.45)2H, 2d, $^2J_{HH}$ = 18 Hz, CH_2(, 3.84)3H, s, OCH_3(, 7.12 (1H, s, CH), 7.05 and 7.54 (4H, 2d, $^3J_{HH}$ = 9 Hz, Ar). ^{13}C NMR (75.5 MHz, acetone-d_6): δ 39.8 (CH_2), 55.7 (OCH_3), 98.6 (CH), 114.9 (C_{meta} of C_6H_4), 126.2 (C_{ortho} of C_6H_4), 129.1 (C_{ipso}), 162.4 (*C*−OCH_3), 165.3 (2C=O).

2-(4-flourophenyl)-1,3-dioxane-4,6-dione (2e). White powder, mp 170 °C. FT-IR)KBr) (υ_{max}, cm^{-1}): 1805, 1768 (C=O). Anal. Calcd for $C_{10}H_7FO_4$)210.16); C, 57.15; H, 3.36%; Found: C, 57.06; H, 3.33%. ^{1}H NMR)300.1 MHz, acetone-d_6): δ 3.63 and 4.59)2H, 2d, $^2J_{HH}$ = 18 Hz, CH_2(, 7.21(1H, s, CH), 7.30 (2H, dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HF}$ = 8.7 Hz, CH_{meta}), 7.70 (2H, dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HF}$ = 5.3 Hz, CH_{ortho}). ^{13}C NMR (75.5 MHz, acetone-d_6): δ 39.8 (CH_2), 97.8 (CH), 116.6 (d, $^2J_{CF}$ = 22.3 Hz, C_{meta} of C_6H_4), 130.0 (d, $^3J_{CF}$ = 8.8 Hz, C_{ortho} of C_6H_4), 130.5 (C_{ipso}), 164.7 (d, $^1J_{CF}$ = 249 Hz, C−F), 164.9 (2C=O).

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General Procedure for Preparation of 3a–j(Exemplified by 3a)

Dimethyl 2-[5-(2-phenyl-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phospha nylidene)-succinate (3a). A mixture of dimethyl acetylenedicarboxylate **1a** (0.12 mL, 1 mmol) in ethyl acetate (2 mL) was added dropwise at room temperature over 10 min to a magnetically stirred solution of **2a** (0.212 g, 1 mmol) and triphenyl phosphine (0.26 g, 1 mmol) in ethyl acetate (10 mL). The mixture was allowed to stand at room temperature (25 °C) along with stirring for 1 h. The resulting mixture was filtered to give ylide **3a** as a white powder. mp 150 °C, and yield 81%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1633, 1695, and 1732 (C=O). Anal. Calcd for $C_{34}H_{29}O_8P$ (596.16); C, 68.45; H, 4.90%. Found: C, 68.33; H, 4.88%.

Major isomer (*E*)-**3a** (55%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.23 and 3.28 (6H, 2s, $2OCH_3$), 4.75 (1H, dd, $^4J_{PH}$ = 4.0 Hz, $^3J_{HH}$ = 11 Hz, $CH(C{=}O)_2$), 5.67 (1H, dd, $^3J_{PH}$ = 11 Hz, $^3J_{HH}$ = 11 Hz, P−C−*C*H), 6.27 (1H, s, Ar−CH), 7.25–7.85 (20H, m, 4 Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 43.5 (d, $^1J_{PC}$ = 91.3 Hz, P−C), 44.1 (P−C−*C*H), 52.6 and 53.0 ($2OCH_3$), 72.2 (*C*H(C=O)$_2$), 96.1 (*C*H−Ar), 121.3 (d, $^1J_{PC}$ = 83.8 Hz, C_{ipso}), 126.5, 127.9, 128.7, and 135.9 (Ar), 129.4 (d, $^3J_{PC}$ = 12.9 Hz, C_{meta}), 134.2 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 133.8 (d, $^4J_{PC}$ = 2.9 Hz, C_{para}), 167.6 (C=O), 168.3 (d, $^2J_{PC}$ = 26.4 Hz, P−C=*C*), 174.0 (*C*O_2CH_3). ^{31}PNMR (121.5 MHz, $CDCl_3$): δ 23.2 (Ph_3P^+−*C*).

Minor isomer (*Z*)-**3a** (45%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.29 and 3.60 (6H, 2s, $2OCH_3$), 4.66 (1H, dd, $^4J_{PH}$ = 7.0 Hz, $^3J_{HH}$ = 11.7 Hz, $CH(C{=}O)_2$), 5.76 (1H, dd, $^3J_{PH}$ = 13.6 Hz, $^3J_{HH}$ = 11.7 Hz, P−C−*C*H), 5.29 (1H, s, Ar−CH), 7.25–7.85 (20H,m, 4 Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 43.1 (d, $^1J_{PC}$ = 52.1 Hz, P−C), 44.6 (P−C−*C*H), 52.8 and 53.4 ($2OCH_3$), 72.7 (*C*H(C=O)$_2$), 94.9 (*C*H−Ar), 118.1 (d, $^1J_{PC}$ = 80.5 Hz, C_{ipso}), 126.4, 127.8, 128.8, and 136.5 (Ar), 129.8 (d, $^3J_{PC}$ = 12.8 Hz, C_{meta}), 134.1 (d, $^2J_{PC}$ = 9.9 Hz,

C_{ortho}), 134.6 (d, $^4J_{PC}$ = 3 Hz, C_{para}), 167.1 (C=O), 167.7 (d, $^2J_{PC}$ = 22.6 Hz, P−C=*C*), 173.9 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 (Ph_3P^+−*C*).

Dimethyl 2-[5-(2-(4-chlorophenyl)-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3b). White powder, mp 146 °C, and yield 65%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1750, 1726, 1690, and 1623 (C=O). Anal. Calcd for $C_{34}H_{29}ClO_8P$ (630.12); C, 64.72; H, 4.47%; Found: C, 64.72; H, 4.59%.

Major isomer (*E*)-**3b** (55%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.22 and 3.27 (6H, 2s, 2OCH_3), 4.72 (1H, dd, $^3J_{HH}$ = 11 Hz, $^4J_{PH}$ = 4.0 Hz, CH(C=O)$_2$), 5.65 (1H, dd, $^3J_{HH}$ = 11 Hz, $^3J_{PH}$ = 11 Hz, P−C−*C*H), 6.24 (1H, s, Ar−CH), 7.25–7.84 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 43.4 (d, $^1J_{PC}$ = 92.8 Hz, P−C), 44.0 (P−C−*C*H), 52.7 and 53.0 (2OCH_3), 72.2 (*C*H(C=O)$_2$), 95.4 (*C*H−Ar), 121.3 (d, $^1J_{PC}$ = 88.3 Hz, C_{ipso}), 128.0, 128.2, 134.6, and 135.2 (Ar), 129.4 (d, $^3J_{PC}$ = 12.2 Hz, C_{meta}), 134.2 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 133.8 (d, $^4J_{PC}$ = 2.3 Hz, C_{para}), 168.1 (d, $^2J_{PC}$ = 20.1 Hz, P−C=*C*), 167.6 (C=O), 173.9 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 (Ph_3P^+−C).

Minor isomer (*Z*)-**3b** (45%), ^{1}H NMR (300.1 MHz, $CDCL_3$: δ 3.30 and 3.60 (6H, 2s, 2OCH_3), 4.66 (1H, dd, $^3J_{HH}$ = 11.6 Hz, $^4J_{PH}$ = 7.0 Hz, CH(C=O)$_2$), 5.76 (1H, dd, $^3J_{HH}$ = 11.6 Hz, $^3J_{PH}$ = 13.6 Hz, P−C−*C*H), 5.28 (1H, s, Ar−CH), 7.25–7.84 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 43.2 (d, $^1J_{PC}$ = 52.8 Hz, P−C), 44.6 (P−C−*C*H), 52.8 and 53.4 (2OCH_3), 72.8 (*C*H(C=O)$_2$), 94.2 (*C*H−Ar), 118.0 (d, $^1J_{PC}$ = 86.8 Hz, C_{ipso}), 127.8, 128.1, 134.4, and 135.0 (Ar), 129.8 (d, $^3J_{PC}$ = 15.1 Hz, C_{meta}), 134.1 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 134.6 (d, $^4J_{PC}$ = 2.3 Hz, C_{para}), 167.4 (d, $^2J_{PC}$ = 17.5 Hz, P−C=*C*), 166.8 (C=O), 173.7 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.4 (Ph_3P^+−C).

Dimethyl 2-[5-(2-(4-methylphenyl)-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3c). White powder, mp 140 °C, and yield 63%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1729, 1612, and 1685 (C=O). Anal. Calcd for $C_{35}H_{31}O_8P$ (610.18); C, 68.85; H, 5.12%; Found: C, 68.82; H, 4.90%.

Major isomer (*E*)-**3c** (55%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.33 (3H, s, CH_3), 3.24 and 3.29 (6H, 2s, 2OCH_3), 4.76 (1H, dd, $^3J_{HH}$ = 11 Hz, $^4J_{PH}$ = 4.0 Hz, CH(C=O)$_2$), 5.68 (1H, dd, $^3J_{HH}$ = 11 Hz, $^3J_{PH}$ = 11 Hz, P−C−*C*H), 6.25 (1H, s, Ar−CH), 7.07–7.88 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 21.2 (CH_3), 43.5 (d, $^1J_{PC}$ = 92.0 Hz, P−C), 44.1 (P−C−*C*H), 52.7 and 53.0 (2OCH_3), 72.3 (*C*H(C=O)$_2$), 95.0 (*C*H−Ar), 121.4 (d, $^1J_{PC}$ = 90.5 Hz, C_{ipso}), 126.3, 128.5, 133.7, and 138.6 (Ar), 129.4 (d, $^3J_{PC}$ = 14.3 Hz, C_{meta}), 134.3 (d, $^2J_{PC}$ = 6.0 Hz, C_{ortho}), 134.3 (d, $^4J_{PC}$ = 2.3 Hz, C_{para}), 168.4 (d, $^2J_{PC}$ = 39.3 Hz, P−C=*C*), 167.7 (C=O), 174.0 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.2 (Ph_3P^+−C).

Minor isomer (*Z*)-**3c** (45%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.30 (3H, s, CH_3), 3.31 and 3.61 (6H, 2s, 2OCH_3), 4.67 (1H, dd, $^3J_{HH}$ = 11.6 Hz, $^4J_{PH}$ = 7.0 Hz, CH(C=O)$_2$), 5.78 (1H, dd, $^3J_{HH}$ = 11.6 Hz, $^3J_{PH}$ = 13.6 Hz, P−C−*C*H), 5.27 (1H, s, Ar−CH), 7.07–7.88 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 21.2 (CH_3), 43.4 (d, $^1J_{PC}$ = 52.1 Hz, P−C), 44.7 (P−C−*C*H), 52.9 and 53.4 (2OCH_3), 72.8 (*C*H(C=O)$_2$), 96.2 (*C*H−Ar), 118.2 (d, $^1J_{PC}$ = 90.5 Hz, C_{ipso}), 126.5, 128.6, 133.1, and 138.5 (Ar), 129.8 (d, $^3J_{PC}$ = 13.6 Hz, C_{meta}), 134.2 (d, $^2J_{PC}$ = 6.0 Hz, C_{ortho}), 133.8 (d, $^4J_{PC}$ = 2.3 Hz, C_{para}), 167.4 (d, $^2J_{PC}$ = 24.1 Hz, P−C=*C*), 167.2 (C=O), 173.6 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 (Ph_3P^+−C).

Dimethyl 2-[5-(2-(4-methoxyphenyl)-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3d). White powder, mp 158 °C, and yield 71%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1752, 1726, 1686, and 1620 (C=O). Anal. Calcd for $C_{35}H_{31}O_9P$ (626.17); C, 67.09; H, 4.99%; Found: C, 66.92; H, 5.18%.

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Major isomer (*E*)-**3d** (54%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.24, 3.29, and 3.78 (9H, 3s, $3OCH_3$), 4.75 (1H, dd, $^{3}J_{HH} = 11$ Hz, $^{4}J_{PH} = 4.0$ Hz, $CH(C{=}O)_2$), 5.67 (1H, dd, $^{3}J_{HH} = 11$ Hz, $^{3}J_{PH} = 11$ Hz, P−C−*C*H), 6.23 (1H, s, Ar−CH), 7.25–7.88 (19H, m, Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 43.5 (d, $^{1}J_{PC} = 91.3$ Hz, P−C), 44.1 (P−C−*C*H), 52.7, 53.0, and 55.2 ($3OCH_3$), 72.2 (*C*H(C=O)$_2$), 96.2 (*C*H−Ar), 121.4 (d, $^{1}J_{PC} = 90.5$ Hz, C_{ipso}), 113.3, 127.8, 129.0, and 159.9 (Ar), 129.4 (d, $^{3}J_{PC} = 15.0$ Hz, C_{meta}), 134.2 (d, $^{2}J_{PC} = 9.8$ Hz, C_{ortho}), 133.8 (d, $^{4}J_{PC} = 2.3$ Hz, C_{para}), 168.4 (d, $^{2}J_{PC} = 39.3$ Hz, P−C=*C*), 167.6 (C=O), 174.0 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 (Ph_3P^+−*C*).

Minor isomer (*Z*)-**3d** (46%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.30, 3.61, and 3.77 (9H, 3s, $3OCH_3$), 4.66 (1H, dd, $^{3}J_{HH} = 11.6$ Hz, $^{4}J_{PH} = 7.0$ Hz, $CH(C{=}O)_2$), 5.77 (1H, dd, $^{3}J_{HH} = 11.6$ Hz, $^{3}J_{PH} = 13.6$ Hz, P−C−*C*H), 5.24 (1H, s, Ar−CH), 7.25–7.88 (19H, m, Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 43.4 (d, $^{1}J_{PC} = 52.1$ Hz, P−C), 44.6 (P−C−*C*H), 52.6, 54.8, and 55.1 ($3OCH_3$), 72.7 (*C*H(C=O)$_2$), 94.9 (*C*H−Ar), 118.1 (d, $^{1}J_{PC} = 90.5$ Hz, C_{ipso}), 113.1, 127.9, 128.4, and 160.0 (Ar), 129.7 (d, $^{3}J_{PC} = 15.0$ Hz, C_{meta}), 134.1 (d, $^{2}J_{PC} = 9.9$ Hz, C_{ortho}), 134.6 (d, $^{4}J_{PC} = 2.3$ Hz, C_{para}), 167.8 (d, $^{2}J_{PC} = 22.8$ Hz, P−C=*C*), 167.2 (C=O), 174.0 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 (Ph_3P^+−*C*).

Dimethyl 2-[5-(2-(4-flourophenyl)-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3e). White powder, mp 162 °C, and yield 50%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1734, 1719, and 1627 (C=O). Anal. Calcd for $C_{34}H_{28}FO_8P$ (614.15); C, 66.45; H, 4.59%; Found: C, 66.41; H, 4.48%.

Major isomer (*E*)-**3e** (58%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 3.24 and 3.29 (6H, 2s, $2OCH_3$), 4.75 (1H, dd, $^{3}J_{HH} = 11$ Hz, $^{4}J_{PH} = 4.0$ Hz, $CH(C{=}O)_2$), 5.66 (1H, dd, $^{3}J_{HH} = 11$ Hz, $^{3}J_{PH} = 11$ Hz, P−C−*C*H), 6.26 (1H, s, Ar−CH), 7.00 (2H, dd, $^{3}J_{HH} = 9$ Hz, $^{3}J_{HF} = 8.7$ Hz, CH_{meta} of C_6H_4F), 7.25 (2H, dd, $^{3}J_{HH} = 9$ Hz, $^{4}J_{HF} = 5.3$ Hz, CH_{ortho} of C_6H_4F), 7.58–7.86 (15H, m, 3Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 43.5 (d, $^{1}J_{PC} = 91.3$ Hz, P−C), 44.1 (P−C−*C*H), 52.6 and 53.0 ($2OCH_3$), 72.2 (*C*H(C=O)$_2$), 95.6 (*C*H−Ar), 121.3 (d, $^{1}J_{PC} = 88.3$ Hz, C_{ipso}), 114.9 (d, $^{2}J_{CF} = 21.7$ Hz, C_{meta} of C_6H_4F), 128.5 (d, $^{3}J_{CF} = 8.3$ Hz, C_{ortho} of C_6H_4F), 129.5 (d, $^{3}J_{PC} = 12.8$ Hz, C_{meta}), 132.6 (C_{ipso} of C_6H_4F), 133.9 (d, $^{4}J_{PC} = 2.3$ Hz, C_{para}), 134.2 (d, $^{2}J_{PC} = 9.8$ Hz, C_{ortho}), 163.0 (d, $^{1}J_{CF} = 241.5$ Hz, C−F), 168.2 (d, $^{2}J_{PC} = 22.6$ Hz, P−C=*C*), 167.6 (C=O), 174.0 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 (Ph_3P^+−*C*).

Minor isomer (*Z*)-**3e** (42%), ^{1}H NMR (300.1 MHz, $CDCl_3$): 3.31 and 3.61 (6H, 2s, $2OCH_3$), 4.68 (1H, dd, $^{3}J_{HH} = 11.6$ Hz, $^{4}J_{PH} = 7.0$ Hz, $CH(C{=}O)_2$), 5.78 (1H, dd, $^{3}J_{HH} = 11.6$ Hz, $^{3}J_{PH} = 13.6$ Hz, P−C−*C*H), 5.29 (1H, s, Ar−CH), 6.98 (2H, dd, $^{3}J_{HH} = 9$ Hz, $^{3}J_{HF} = 8.7$ Hz, CH_{meta} of C_6H_4F), 7.32 (2H, dd, $^{3}J_{HH} = 9$ Hz, $^{4}J_{HF} = 5.3$ Hz, CH_{ortho} of C_6H_4F), 7.58–7.91 (15H, m, 3Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 43.4 (d, $^{1}J_{PC} = 52.1$ Hz, P−C), 44.7 (P−C−*C*H), 52.8 and 53.4 ($2OCH_3$), 72.6 (*C*H(C=O)$_2$), 94.4 (*C*H−Ar), 118.1 (d, $^{1}J_{PC} = 86.0$ Hz, C_{ipso}), 114.8 (d, $^{2}J_{CF} = 21.7$ Hz, C_{meta} of C_6H_4F), 128.4 (d, $^{3}J_{CF} = 8.3$ Hz, C_{ortho} of C_6H_4F), 132.5 (C_{ipso} of C_6H_4F), 162.9 (d, $^{1}J_{CF} = 241.5$ Hz, C−F), 129.8 (d, $^{3}J_{PC} = 12.8$ Hz, C_{meta}), 134.1 (d, $^{2}J_{PC} = 10.6$ Hz, C_{ortho}), 134.1 (d, $^{4}J_{PC} = 2.3$ Hz, C_{para}), 167.5 (d, $^{2}J_{PC} = 16.5$ Hz, P−C=*C*), 166.9 (C=O), 173.7 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.4 (Ph_3P^+−*C*).

Diethyl 2-[5-(2-phenyl-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3f). White powder, mp 156 °C., and yield 72%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1744, 1717, 1685, 1616 (C=O). Anal. Calcd for $C_{36}H_{33}O_8P$ (624.19); C, 69.22; H, 5.33%; Found: C, 69.02; H, 5.27%.

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Major isomer (*E*)-**3f** (64%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.84 and 0.98 (6H, 2t, $^3J_{HH} = 7.1$ Hz, $2CH_3$), 3.60 and 3.76 (4H, 2q, $^3J_{HH} = 7.1$ Hz, $2OCH_2CH_3$), 4.76 (1H, dd, $^3J_{HH} = 11$ Hz, $^4J_{PH} = 3.4$ Hz, $CH(C{=}O)_2$), 5.60 (1H, dd, $^3J_{HH} = 11$ Hz, $^3J_{PH} = 11$ Hz, P−C−*C*H), 5.38 (1H, s, Ar−CH), 7.25–7.92 (20H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.6 and 13.7 (OCH_2CH_3), 43.6 (d, $^1J_{PC} = 138.8$ Hz, P−C), 44.5 (P−C−*C*H), 61.7 and 62.8 ($2OCH_2CH_3$), 72.2 (*C*H(C=O)$_2$), 96.1 (*C*H−Ar), 122.3 (d, $^1J_{PC} = 89.0$ Hz, C_{ipso}), 126.6, 127.9, 128.8, and 136.6 (Ar), 129.4 (d, $^3J_{PC} = 12.8$ Hz, C_{meta}), 134.3 (d, $^2J_{PC} =$ 9.7 Hz C_{ortho}), 133.7 (d, $^4J_{PC} = 3.1$ Hz, C_{para}), 168.5 (d, $^2J_{PC} = 37.7$ Hz, P−C=*C*), 167.3 (C=O), 173.6 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.1 (Ph_3P^+−*C*).

Minor isomer (*Z*)-**3f** (36%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.93 and 1.16 (6H, 2t, $^3J_{HH} = 7.1$ Hz, $2CH_3$), 4.10 and 4.16 (4H, q, $^3J_{HH} = 7.1$ Hz, $2OCH_2CH_3$), 4.71 (1H, dd, $^3J_{HH} = 11.7$ Hz, $^4J_{PH} = 6.8$ Hz, $CH(C{=}O)_2$), 5.83 (1H, dd, $^3J_{HH} = 11.7$ Hz, $^3J_{PH} = 14.2$ Hz, P−C−*C*H), 5.28 (1H, s, Ar−CH), 7.25–7.92 (20H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.4 and 14.1 (OCH_2CH_3), 43.4 (d, $^1J_{PC} = 60.4$ Hz, P−C), 44.7 (P−C−*C*H), 61.4 and 62.2 ($2OCH_2CH_3$), 72.6 (*C*H(C=O)$_2$), 94.9 (*C*H−Ar), 118.8 (d, $^1J_{PC} = 90.5$ Hz, C_{ipso}), 126.4, 127.8, 128.8, and 136.4 (Ar), 129.7 (d, $^3J_{PC} = 15.1$ Hz, C_{meta}), 134.2 (d, $^2J_{PC} =$ 9.7 Hz C_{ortho}), 134.5 (d, $^4J_{PC} = 3.1$ Hz C_{para}), 167.5 (d, $^2J_{PC} = 24.1$ Hz, P−C=*C*), 167.2 (C=O), 173.6 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 (Ph_3P^+−*C*).

Diethyl 2-[5-(2-(4-chlorophenyl)-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3g). White powder, mp 154 °C, and yield 66%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1744, 1718, 1689, and 1621 (C=O). Anal. Calcd for $C_{36}H_{32}ClO_8P$ (658.15); C, 65.61; H, 4.89%; Found: C, 65.49; H, 4.89%.

Major isomer (*E*)-**3g** (64%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.83 and 0.97 (6H, 2t, $^3J_{HH} = 7.1$ Hz, $2CH_3$), 3.60 and 3.73 (4H, q, $^3J_{HH} = 7.1$ Hz, $2OCH_2CH_3$), 4.74 (1H, dd, $^3J_{HH} = 11$ Hz, $^4J_{PH} = 3.4$ Hz, $CH(C{=}O)_2$), 5.56 (1H, dd, $^3J_{HH} = 11$ Hz, $^3J_{PH} = 11$ Hz, P−C−*C*H), 6.27 (1H, s, Ar−CH), 7.25–7.86 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.6 and 13.7 (OCH_2CH_3), 43.6 (d, $^1J_{PC} = 138.8$ Hz, P−C), 44.5 (P−C−*C*H), 61.8 and 62.8 ($2OCH_2CH_3$), 72.2 (*C*H(C=O)$_2$), 95.4 (*C*H−Ar), 121.2 (d, $^1J_{PC} = 89.0$, C_{ipso}), 128.0, 128.2,134.5, and 135.0 (Ar), 129.4 (d, $^3J_{PC} = 12.8$ Hz, C_{meta}), 134.2 (d, $^2J_{PC} =$ 9.9 Hz C_{ortho}), 133.8 (d, $^4J_{PC} = 3.0$ Hz C_{para}), 168.1 (d, $^2J_{PC} = 37.0$ Hz, P−C=*C*), 167.2 (C=O), 173.4 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 22.7 (Ph_3P^+−*C*).

Minor isomer (*Z*)-**3g** (36%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.92 and 1.18 (6H, 2t, $^3J_{HH} = 7.1$ Hz, $2CH_3$), 3.85 and 3.99 (4H, q, $^3J_{HH} = 7.1$ Hz, $2OCH_2CH_3$), 4.60 (1H, dd, $^3J_{HH} = 11.7$ Hz, $^4J_{PH} = 6.8$ Hz, $CH(C{=}O)_2$), 5.66 (1H, dd, $^3J_{HH} = 11.7$ Hz, $^3J_{PH} = 14.2$ Hz, P−C−*C*H), 5.13 (1H, s, Ar−CH), 7.25–7.86 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.3 and 14.1 (OCH_2CH_3), 43.4 (d, $^1J_{PC} = 60.4$ Hz, P−C), 44.7 (P−C−*C*H), 61.4 and 62.3 ($2OCH_2CH_3$), 72.6 (*C*H(C=O)$_2$), 94.6 (*C*H−Ar), 118.1 (d, $^1J_{PC} = 86.5$ Hz, C_{ipso}), 127.8, 128.1, 134.7, and 135.3 (Ar), 129.7 (d, $^3J_{PC} = 12.8$ Hz, C_{meta}), 134.3 (d, $^2J_{PC} =$ 9.9 Hz C_{ortho}), 134.5 (d, $^4J_{PC} = 3.1$ Hz C_{para}), 167.5 (d, $^2J_{PC} = 24.5$ Hz, P−C=*C*), 167.2 (C=O), 173.4 (CO_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 (Ph_3P^+−*C*).

Diethyl 2-[5-(2-(4-methylphenyl)-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3h). White powder, mp 175 °C, and yield 78%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1740, 1718, 1684, and 1616 (C=O). Anal. Calcd for $C_{37}H_{35}O_8P$ (638.64); C, 69.58; H, 5.52%; Found: C, 69.44; H, 5.36.

Major isomer (*E*)-**3h** (67%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.83 and 0.97 (6H, 2t, $^3J_{HH} = 7.1$ Hz, $2CH_3$), 2.32 (3H, s, CH_3), 3.57 and 3.73 (4H, q, $^3J_{HH} = 7.1$ Hz, $2OCH_2CH_3$), 4.75 (1H, dd, $^3J_{HH} = 11$ Hz, $^4J_{PH} = 3.4$ Hz, $CH(C{=}O)_2$), 5.58 (1H, dd, $^3J_{HH} =$ 11 Hz, $^3J_{PH} = 11$ Hz, P−C−*C*H), 6.27 (1H, s, Ar−CH), 7.06–7.90 (19H, m, 4Ar). ^{13}C

NMR (75.46 MHz, $CDCl_3$): δ 13.6 and 13.7 ($2OCH_2\mathit{C}H_3$), 21.2 (CH_3), 43.6 (d, $^1J_{PC}$ = 138.8 Hz, P−C), 44.5 (P−C−*C*H), 61.7 and 62.8 ($2O\mathit{C}H_2CH_3$), 72.2 (*C*H(C=O)$_2$), 96.2 (*C*H−Ar), 121.8 (d, $^1J_{PC}$ = 89.0, C_{ipso}), 126.4, 128.6, 133.1, and 138.5 (Ar), 129.4 (d, $^3J_{PC}$ = 12.8 Hz, C_{meta}), 134.2 (d, $^2J_{PC}$ = 9.8 Hz C_{ortho}), 133.7 (d, $^4J_{PC}$ = 2.9 Hz C_{para}), 168.3 (d, $^2J_{PC}$ = 42.9, P−C=*C*), 167.3 (C=O), 173.5 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.1 (Ph_3P^+−*C*).

Minor isomer (*Z*)-**3h** (33%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.92 and 1.15 (6H, 2t, $^3J_{HH}$ = 7.1 Hz, $2CH_3$), 2.29 (3H, s, CH_3), 4.04 and 4.11 (4H, q, $^3J_{HH}$ = 7.1 Hz, $2OCH_2CH_3$), 4.67 (1H, dd, $^3J_{HH}$ = 11.7 Hz, $^4J_{PH}$ = 6.8 Hz, CH(C=O)$_2$), 5.80 (1H, dd, $^3J_{HH}$ = 11.7 Hz, $^3J_{PH}$ = 14.2 Hz, P−C−*C*H), 5.31 (1H, s, Ar−CH), 7.06–7.90 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.3 and 14.0 ($OCH_2\mathit{C}H_3$), 21.2 (CH_3), 43.4 (d, $^1J_{PC}$ = 60.4 Hz, P−C), 44.7 (P−C−*C*H), 61.4 and 62.2 ($2O\mathit{C}H_2CH_3$), 72.6 (*C*H(C=O)$_2$), 95.0 (*C*H−Ar), 118.2 (d, $^1J_{PC}$ = 86.8 Hz, C_{ipso}), 126.3, 128.5, 133.2, and 138.5 (Ar), 129.7 (d, $^3J_{PC}$ = 12.8 Hz, C_{meta}), 134.3 (d, $^2J_{PC}$ = 9.8 Hz C_{ortho}), 134.5 (d, $^4J_{PC}$ = 2.9 Hz, C_{para}), 167.6 (d, $^2J_{PC}$ = 23.8 Hz, P−C=*C*), 167.2 (C=O), 173.3 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.2 (Ph_3P^+−*C*).

Diethyl 2-[5-(2-(4-methoxyphenyl)-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3i). White powder, mp 155 °C, and yield 77%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1744, 1715, 1686, and 1616 (C=O). Anal. Calcd for $C_{37}H_{35}O_9P$ (654.64); C, 67.88; H, 5.39%; Found: C, 67.83; H, 5.24%.

Major isomer (*E*)-**3i** (64%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.83 and 0.98 (6H, 2t, $^3J_{HH}$ = 7.1 Hz, $2CH_3$), 3.78 (3H, s, OCH_3), 3.59 and 3.75 (4H, q, $^3J_{HH}$ = 7.1 Hz, $2O\mathit{C}H_2CH_3$), 4.75 (1H, dd, $^3J_{HH}$ = 11 Hz, $^4J_{PH}$ = 3.4 Hz, CH(C=O)$_2$), 5.58 (1H, dd, $^3J_{HH}$ = 11 Hz, $^3J_{PH}$ = 11 Hz, P−C−*C*H), 6.26 (1H, s, Ar−CH), 6.85–7.86 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.6 and 13.7 ($2OCH_2\mathit{C}H_3$), 43.6 (d, $^1J_{PC}$ = 138.8 Hz, P−C), 44.5 (P−C−*C*H), 55.2 (OCH_3), 61.7 and 62.8 ($2O\mathit{C}H_2CH_3$), 72.2 (*C*H(C=O)$_2$), 96.1 (*C*H−Ar), 121.9 (d, $^1J_{PC}$ = 89.0 Hz, C_{ipso}), 113.3, 127.9, 129.0, and 159.9 (Ar), 129.4 (d, $^3J_{PC}$ = 12.8 Hz, C_{meta}), 134.2 (d, $^2J_{PC}$ = 9.8 Hz C_{ortho}), 133.7 (d, $^4J_{PC}$ = 2.8 Hz C_{para}), 168.3 (d, $^2J_{PC}$ = 42.9, P−C=*C*), 167.3 (C=O), 173.5 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.1 (Ph_3P^+−*C*).

Minor isomer (*Z*)-**3i** (36%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.92 and 1.15 (6H, 2t, $^3J_{HH}$ = 7.1 Hz, $2CH_3$), 3.76 (3H, s, OCH_3), 4.06 and 4.12 (4H, q, $^3J_{HH}$ = 7.1 Hz, $2O\mathit{C}H_2CH_3$), 4.69 (1H, dd, $^3J_{HH}$ = 11.7 Hz, $^4J_{PH}$ = 6.8 Hz, CH(C=O)$_2$), 5.80 (1H, dd, $^3J_{HH}$ = 11.7 Hz, $^3J_{PH}$ = 14.2 Hz, P−C−*C*H), 5.30 (1H, s, Ar−CH), 6.85–7.86 (19H, m, 4Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.3 and 14.1 ($OCH_2\mathit{C}H_3$), 43.4 (d, $^1J_{PC}$ = 60.4 Hz, P−C), 44.7 (P−C−*C*H), 55.2 (OCH_3), 61.4 and 62.2 ($2O\mathit{C}H_2CH_3$), 72.6 (*C*H(C=O)$_2$), 94.9 (*C*H−Ar), 118.3 (d, $^1J_{PC}$ = 86.0 Hz, C_{ipso}), 113.1, 127.8, 128.4, and 160.1 (Ar), 129.7 (d, $^3J_{PC}$ = 12.8 Hz, C_{meta}), 134.3 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 134.5 (d, $^4J_{PC}$ = 2.8 Hz, C_{para}), 167.5 (d, $^2J_{PC}$ = 23.8, P−C=*C*), 167.2 (C=O), 173.5 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.2 (Ph_3P^+−*C*).

Diethyl 2-[5-(2-(4-flourophenyl)-1,3-dioxane-4,6-dion)]-3(Triphenyl-λ^5-phosphanylidene)-succinate (3j). White powder, mp 146 °C, and yield 53%. FT-IR (KBr) (υ_{max}, cm^{-1}): 1743, 1717, 1688, and 1620 (C=O). Anal. Calcd for $C_{36}H_{32}FO_8P$ (642.61); C, 67.29; H, 5.02%; Found: C, 67.29; H, 5.0%.

Major isomer (*E*)-**3j** (67%), ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 0.83 and 0.97 (6H, 2t, $^3J_{HH}$ = 7.1 Hz, $2CH_3$), 3.60 and 3.73 (4H, q, $^3J_{HH}$ = 7.1 Hz, $2O\mathit{C}H_2CH_3$), 4.75 (1H, dd, $^3J_{HH}$ = 11 Hz, $^4J_{PH}$ = 3.4 Hz, CH(C=O)$_2$), 5.56 (1H, dd, $^3J_{HH}$ = 11 Hz, $^3J_{PH}$ = 11 Hz, P−C−*C*H), 6.27 (1H, s, Ar−CH), 7.01 (2H, dd, $^3J_{HH}$ = 8.7 Hz, $^3J_{HF}$ = 9 Hz, CH_{meta} of

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C_6H_4F), 7.25 (2H, dd, $^3J_{HH} = 9$ Hz, $^4J_{HF} = 5.3$ Hz, CH_{ortho} of C_6H_4F), 7.58–7.91 (15H, m, 3Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.6 and 13.7 ($2OCH_2\mathit{C}H_3$), 43.6 (d, $^1J_{PC} =$ 138.8 Hz, P−C), 44.5 (P−C−*C*H), 61.8 and 62.8 ($2O\mathit{C}H_2CH_3$), 72.2 (*C*H(C=O)$_2$), 95.6 (*C*H−Ar), 121.8 (d, $^1J_{PC} = 89.0$ Hz, C_{ipso}), 114.9 (d, $^2J_{CF} = 21.7$ Hz, C_{meta} of C_6H_4F), 128.5 (d, $^3J_{CF} = 8.3$ Hz, C_{ortho} of C_6H_4F), 129.4 (d, $^3J_{PC} = 12.8$ Hz, C_{meta}), 132.6 (C_{ipso} of C_6H_4F), 134.2 (d, $^2J_{PC} = 9.8$ Hz, C_{ortho}), 133.7 (d, $^4J_{PC} = 2.8$ Hz, C_{para}), 163.0 (d, $^1J_{CF} =$ 241.5 Hz, C−F), 168.6 (d, $^2J_{PC} = 37.7$ Hz, P−C=*C*), 167.4 (C=O), 173.4 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.1 ($Ph_3P^+-\mathit{C}$).

Minor isomer (*Z*)-**3j** (33%), ^1H NMR (300.1 MHz, $CDCl_3$): δ 0.92 and 1.15 (6H, 2t, $^3J_{HH} = 7.1$ Hz, $2CH_3$), 4.06 and 4.12 (4H, q, $^3J_{HH} = 7.1$ Hz, 2 O$\mathit{C}H_2CH_3$), 4.72 (1H, dd, $^3J_{HH} = 11.7$ Hz, $^4J_{PH} = 6.8$ Hz, CH(C=O)$_2$), 5.81 (1H, dd, $^3J_{HH} = 11.7$ Hz, $^3J_{PH} = 14.2$ Hz, P−C−*C*H), 5.34 (1H, s, Ar−CH), 6.95 (2H, dd, $^3J_{HH} = 9$ Hz, $^3J_{HF} = 8.7$ Hz, CH_{meta} of C_6H_4F), 7.32 (2H, dd, $^3J_{HH} = 9$ Hz, $^4J_{HF} = 5.3$ Hz, CH_{ortho} of C_6H_4F), 7.58–7.91 (15H, m, 3Ar). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ 13.3 and 13.6 ($OCH_2\mathit{C}H_3$), 43.4 (d, $^1J_{PC} =$ 60.4 Hz, P−C), 44.7 (P−C−*C*H), 61.4 and 62.3 ($2O\mathit{C}H_2CH_3$), 72.6 (*C*H(C=O)$_2$), 94.4 (*C*H−Ar), 118.3 (d, $^1J_{PC} = 86.0$ Hz, C_{ipso}), 114.8 (d, $^2J_{CF} = 21.7$ Hz, C_{meta} of C_6H_4F), 128.3 (d, $^3J_{CF} = 8.3$Hz, C_{ortho} of C_6H_4F), 129.7 (d, $^3J_{PC} = 12.8$ Hz, C_{meta}), 132.5 (C_{ipso} of C_6H_4F), 134.3 (d, $^2J_{PC} = 9.8$ Hz, C_{ortho}), 134.5 (d, $^4J_{PC} = 2.9$ Hz, C_{para}), 161.5 (d, $^2J_{PC} =$ 24.1 HZ, P−C=*C*), 162.9 (d, $^1J_{CF} = 241.5$ Hz, C−F), 167.5 (d, $^2J_{PC} = 24.1$ Hz, P−C=*C*), 167.2 (C=O), 173.4 (*C*O_2CH_3). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 23.3 ($Ph_3P^+-\mathit{C}$).

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