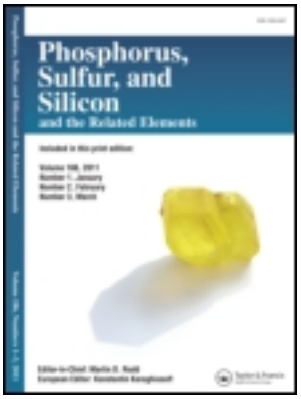

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Synthesis and Dynamic NMR Study of New Stable Ylides Derived from the Reaction of Triphenylphosphine, Dialkyl Acetylenedicarboxylates, and 5-ACYL Meldrum's Acid

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SYNTHESIS AND DYNAMIC NMR STUDY OF NEW STABLE YLIDES DERIVED FROM THE REACTION OF TRIPHENYLPHOSPHINE, DIALKYL ACETYLENEDICARBOXYLATES, AND 5-ACYL MELDRUM'S ACID

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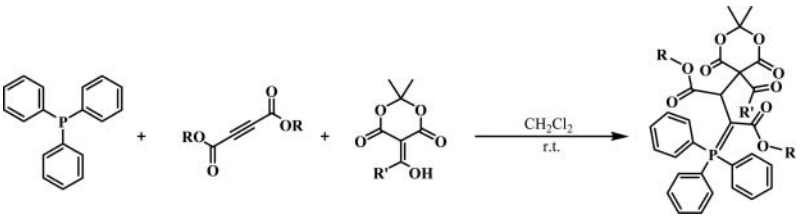
GRAPHICAL ABSTRACT



Abstract *Triphenylphosphine and dialkyl acetylenedicarboxylate react smoothly in the presence of 5-acyl Meldrum's acid in dichloromethane at room temperature and lead to synthesis of new stable ylide derivatives of dimethyl (5-acetyl-2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-yl)-3-(triphenyl-λ^5-phosphanylidene) succinate. Dynamic NMR study results of rotamers are reported and compared with the previous-related reports.*

Keywords Acyl Meldrum's acid; dialkyl acetylenedicarboxylate; three-component reaction; triphenylphosphine; ylide

INTRODUCTION

The extension of simple and fast routes for the synthesis of widely used organic compounds from readily available reagents is one of the major tasks in organic synthesis. Phosphorus compounds are widely used in organic synthesis especially in the synthesis of naturally occurring products and drug compounds.[1–5] Developments of new protocols for the synthesis of physiologically active compounds have not been possible without phosphorus intermediates. Organophosphorus compounds have been of interest for chemists, especially those compounds that can form a new carbon–carbon bond. Due to their susceptibility to participate in further reactions as active intermediates,[6–8] phosphorus ylides are important reagents which take part in interesting and valuable reactions.[9–13] Extensive research has been performed to investigate the reaction between phosphorus and other active reagents

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especially dialkyl acetylenedicarboxylate.[14–17] Recently, the synthesis of new ylides bearing in their structure, suitable functional groups that can react in a Wittig intramolecular reaction, have been described.[18–21]

Meldrum's acid (2,2-dimethyl-1,3-dioxane-4,6-dione) and its derivatives have been broadly used in organic synthesis.[22] It has interesting properties that make it a useful molecule. It is susceptible to nucleophilic and electrophilic attack, undergoing ring-opening reactions, along with high acidity property.[23] A large number of Meldrum's acid derivatives have been used as intermediate in sequential organic synthesis. For instance, they are applied for: preparation of 1,3-dicarbonyl derivatives (using 5-acyl Meldrum's acid),[24] synthesis of different malonic ester derivatives [using 5-mono or dialkyl (aryl) Meldrum's acid],[25] and α-brominated aldehyde or ketones (by 5,5-dibromo Meldrum's acid).[26] Several reports have been published about application of its diverse derived molecules.[22,27,28]

Within our studies on Meldrum's acid and its derivatives in multicomponent reactions[29] herein, the synthesis of new and stable phosphorus ylides based on using 5-acyl Meldrum's acid (5-acyl-2,2-dimethyl-1,3-dioxane-4,6-dione) **3** is reported. The reaction of synthesized acyl Meldrum's acids, triphenylphosphine, and dialkyl acetylenedicarboxylate proceeds at room temperature and leads to new stable phosphorus ylides.

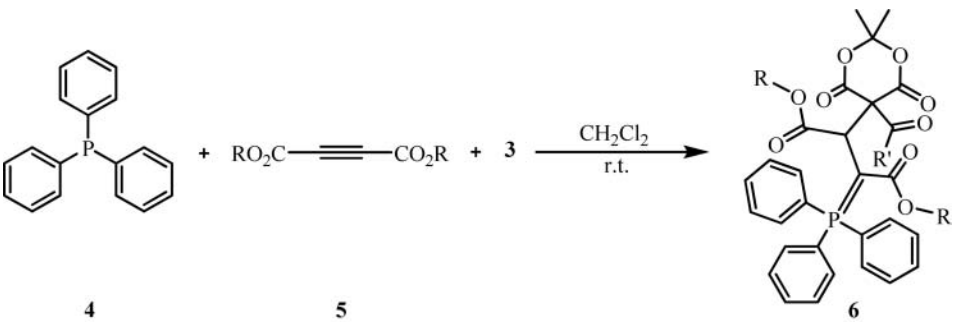
RESULTS AND DISCUSSION

Firstly, acyl Meldrum's acids derivatives were synthesized from the reaction between Meldrum's acid **1** and acyl halides **2** in the presence of pyridine. Obtained products were characterized by their mp, ^{1}H NMR, ^{13}C NMR.[24]

Then, triphenylphosphine **4**, dialkyl acetylenedicarboxylate **5,** and acyl Meldrum's acid **3** readily react in dichloromethane at room temperature. After 2 h the reaction was completed and led to new derivatives of phosphorus ylides **6** in good yields (Scheme 1).

One goal of selecting 5-acyl Meldrum's acid was to investigate the possibility of an internal Wittig reaction after ylide preparation. So, the reaction was continued under various conditions, but the expected reaction did not occur. This fact indicates special stability of synthesized ylides.

The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of phosphorane **6**. Any product other than **6** has not been detected by the NMR spectroscopy.

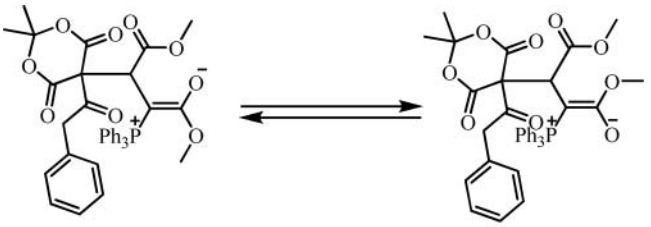


4 5 6

Scheme 1

The structures of products **6a–f** were deduced from their elemental analyses, IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra (as an example, **6a** is represented in Figures S1–S4, Supplemental Materials available online).

The ^{1}H, ^{13}C, and ^{31}P NMR of two products (**6e** and **f**) show the presence of two rotamers; because the structures of these ylides (**6e** and **f**) are strongly conjugated with adjacent carbonyl group and rotation about partial double bond in **6-*E*** and **6-*Z*** geometrical isomers is slow on the NMR time scale at ambient temperature (Scheme 2).



6e (*Z*-Isomer) **6e** (*E*-Isomer)

Scheme 2

^{1}H NMR spectrum of ylides (**6e** and **f**) shows individual signal for two rotamers in the region of CH substructure and OCH_2 (or OCH_3) fragment of ester.

A ^{1}H NMR dynamic study was performed for ylide **6e** in $CDCl_3$ at ambient temperature (30 °C). This spectrum exhibits two sharp doublets for the CH groups of (*E*) and (*Z*) isomers. Increasing the temperature results broaden and coalescence of the CH resonances. At 80 °C, a relatively broad singlet was observed for two CH groups (Figure 1).

The variable temperature spectra allowed calculating the free barrier for the restricted C−C double bond rotation in **6e**. From coalescence temperature of the CH proton resonances and using the expression $k_c = \pi\Delta\nu/\sqrt{2}$, $\Delta G^{\#} = 4.57T_c\ (10.32 + \log T_c/k_c)$, the first-order rate constant (k_c) for the dynamic NMR process in **6e** is 118.5 s^{-1} at 353 K. Application of the absolute rate theory with a transmission coefficient of 1 gives a free-energy

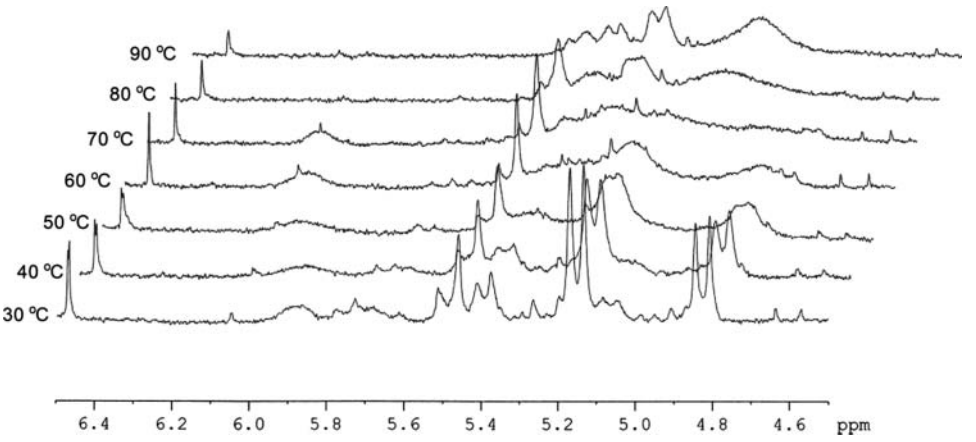


Figure 1 Variable temperature 300 MHz ^{1}H NMR spectra C-H region of **6e** in CD_2Cl_2.

Table 1 Activation parameters for phosphorus ylide rotamers

Compound	T (°C)	(ppm)δ	$\Delta\nu$ (Hz)	k_c (S^{-1})[a]	T_c (K)	$\Delta G^{\#}$ (KJ.mol^{-1})[b]
6e	30	5.95, 6.13	54.02	118.5	353	72.79
	80	6.09				

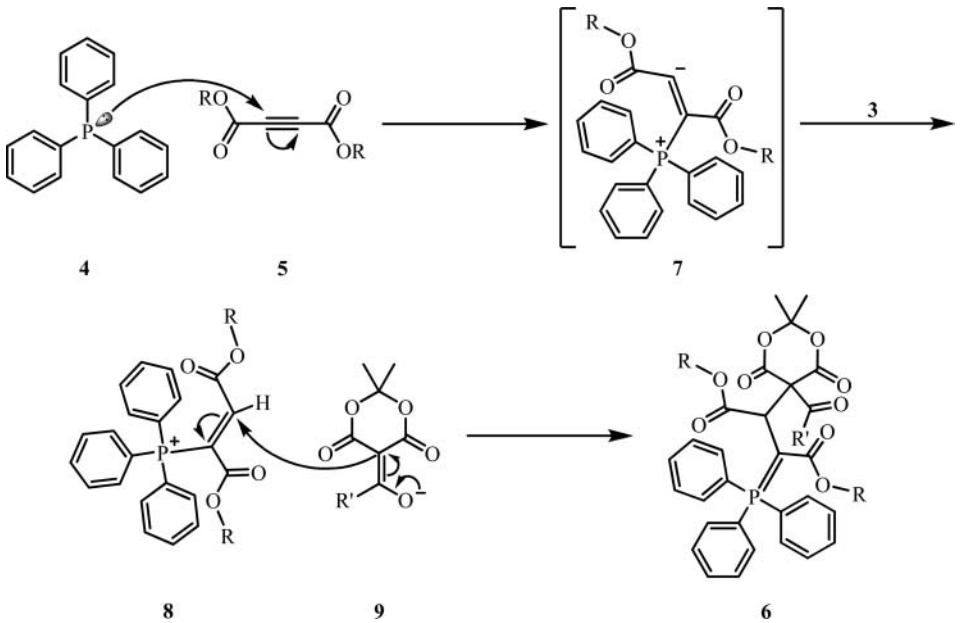
[a]$k_c = \pi\Delta\nu/\sqrt{2}$; [b]$\Delta G^{\#} = 4.57T_c\,(10.32 + \log T_c/k_c)$.

of activation ($\Delta G^{\neq}$) of 72.79 kJ.mol^{-1} (Table 1), where all known sources of errors are estimated and included.

In order to evaluate and contrast these data with previous reports, we compared activation parameters of the some former published data from phosphorus ylide rotamers with our synthesized phosphorus ylides. The result of this comparison is outlined in Table 2. A brief look at the table indicates that different published reports are consistent with each other and prepared ylides have similar stability in rotamers.

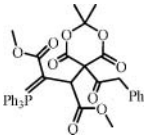
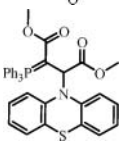
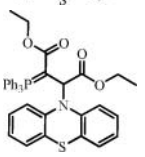
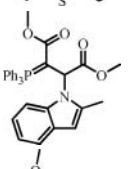
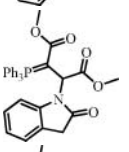
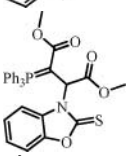
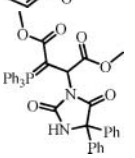
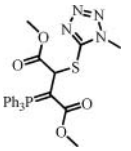
On the basis of the previous reports about this familiar and similar reaction,[30–34] we can propose mechanism of this reaction as follow (Scheme 3). At first, triphenylphosphine **4** attacked to the acetylenic ester **5** and then, protonation of intermediate **7** occurred by acyl Meldrum's acid **3**. Next, resulted anionic carbons **9** add to the positively charged intermediate **8** and formed phosphorane **6** (see Scheme 3).

In conclusion, we described an efficient, simple, and one-pot three-component reaction of triphenylphosphine and dialkyl acetylenedicarboxylate in the presence of 5-acyl Meldrum's acid.



Scheme 3

Table 2 Comparison of rotameric effect (activation parameters) for restricted rotational process around the carbon–carbon double bond between **6e** with other phosphorus ylides

Phosphorus ylide	δ_{CH} (ppm)	$^3J_{PH}$ (Hz)	$\Delta\nu$ (Hz)	k_c (S^{-1})	T_c (K)	$\Delta G^{\#}$ ($KJ.mol^{-1}$)	Ref.
	5.95 6.13	12.02 12.08	54.02	118.50	353	72.8	This work
	4.22 4.28	14.6 15.9	30.00	66.60	298	62.5	[30]
	4.11 4.24	18.5 14.9	65.00	144.40	298	60.6	[30]
	5.15 5.10	—	27.50	61.07	332	70.2 ± 1	[31]
	5.38 5.30	16.4 18.5	15.00	33.00	345	26.0 ± 1	[32]
	5.80 5.65	17.3 19.2	20.00	44.00	336	29.0 ± 1	[32]
	4.58 4.62	15.3 16.6	129.00	286.00	343	68.2 ± 2	[33]
	5.37 5.40	16.7 16.2	15.00	33.32	336	72.7	[34]

EXPERIMENTAL

Melting points were measured on an Electrothermal 9200 apparatus. IR spectra were recorded on a FT-IR 102 MB BOMEM apparatus. Mass spectra were recorded on an AGILENT TECHNOLOGY (HP)-5973 mass spectrometer operating at an ionization potential of 70 eV (EI). ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-300 MHz

spectrometer employing tetramethylsilane as an internal reference. All chemicals and solvents were purchased from Fluka and Merck chemical company and used as received. Table S1 (Supplemental Materials) outlines the scope of synthesis of **6a–f**.

5-acyl Meldrum's acid derivatives **3a–c** were synthesized on the basis of modified literature published procedure (see the Supplemental Materials, available online, for complete details).[24]

*5-(1-Hydroxyethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3a**):* Orange crystals, mp 75–78 °C. Crystallization was performed with ether/hexane, yield 6.9 g, 62%.

*5-(1-Hydroxypropylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3b**):* Yellow crystals, mp 47–50 °C. Crystallization was performed with ether/hexane, yield 8.05 g, 67%.

*5-(1-Hydroxy-2-phenylethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (**3c**):* Pale yellow crystals, mp 87–90 °C. Crystallization was performed with ether/hexane, yield 8.97 g, 57%.

General Procedure for the Preparation of Compounds 6

Exemplified for Dimethyl 2-(5-acetyl-2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-yl)-3-(triphenyl-λ^5-phosphanylidene) succinate (6a). To a stirred solution of triphenylphosphine (0.262 g, 1 mmol) and 5-acetyl-2,2-dimethyl-1,3-dioxane-4,6-dione (0.18 g, 1 mmol) in dichloromethane (10 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.142 g, 1 mmol) in CH_2Cl_2 (2 mL) at room temperature and allowed to stir for 2 h until completion (completion of the reaction was monitored by TLC). The solvent was removed under reduced pressure and the crude product was purified by crystallization in petroleum benzine:diethylether to give **6a** as yellow crystals. Spectra of **6a** are presented in the Supplemental Materials (Figures S1–S4). IR (KBr) (υ_{max}, cm^{-1}): 1735, 1667 (C=O), 1555 (C=C), 1303, 1264, 1190, 1156 (C−O). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 1.67 (6H, s, 2 CH_3), 2.61 (3H, s, CH_3), 3.74 (6H, s, 2 OCH_3), 6.81 (1H, s, CH), 7.39–7.64 (15 H, m, 3 C_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ_C 23.5 (CH_3), 26.6 (2 CH_3), 28.0 (CH), 42.6 (d, $^1J_{PC}$ 128.1 Hz, P=C), 52.1 (2 OCH_3), 91.6 (*C*(C=O)$_3$), 104.6 (*C*(CH_3)$_2$), 122.5 (d, $^1J_{PC}$ 99.0 Hz, C_{ipso}), 128.4 (d, $^3J_{PC}$ 11.0 Hz, C_{meta}), 131.5 (d, $^4J_{PC}$ 2.0 Hz, C_{para}), 134.5 (d, $^2J_{PC}$ 10.0 Hz, C_{ortho}), 165.1 (d, $^3J_{PC}$ 12.8 Hz, C=O ester), 170.5 (d, $^2J_{PC}$ 13.8 Hz, C=O ester), 194.4 (C=O). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ_p 29.4 ppm. Anal. calcd. for $C_{32}H_{31}O_9P$ (590.562): C, 65.08; H, 5.29%. Found: C, 65.17; H, 5.38%. MS: *m/z* (%) = 590 (M^+,1), 515 (5), 429 (8), 405 (7), 368 (10), 332 (8), 293 (10), 278 (32), 277 (74), 262 (100), 236 (8), 201 (18), 183 (72), 152(20), 108 (24), 77 (23), 57 (23), 43 (51).

Diethyl 2-(5-acetyl-2,2-dimethyl-4,6-dioxo-1,3-dioxane-5-yl)-3-(triphenyl-λ^5-phosphanylidene) succinate (6b). IR (KBr) (υ_{max}, cm^{-1}): 1736, 1666 (C=O), 1556 (C=C), 1302, 1263, 1190, 1121 (C−O). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 1.29 (6H, t, $^3J_{HH}$ 7.1 Hz, 2 CH_3), 1.71 (6H, s, 2 CH_3), 2.65 (3 H, s, CH_3), 4.23 (4 H, q, $^3J_{HH}$ 7.1 Hz, 2 CH_2), 6.83 (1 H, s, CH), 7.43–7.68 (15 H, m, 3 C_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ_C 14.1 (2 CH_3), 23.5 (CH_3), 26.8 (2 CH_3), 29.7 (CH), 42.9 (d, $^1J_{PC}$ 128.2 Hz, P=C), 61.3 (2 OCH_2), 91.8 (*C*(C=O)$_3$), 104.9 (*C*(CH_3)$_2$), 123.0 (d, $^1J_{PC}$ 99.2 Hz, C_{ipso}), 128.7 (d, $^3J_{PC}$ 11.0 Hz, C_{meta}), 131.5 (d, $^4J_{PC}$ 2.0 Hz, C_{para}), 134.0 (d, $^2J_{PC}$ 10.2 Hz, C_{ortho}), 165.1 (d, $^4J_{PC}$ 12.8 Hz, C=O ester), 170.3 (d, $^2J_{PC}$ 13.4 Hz, C=O ester), 194.6 (C=O). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ_P 29.3. Anal. calcd. for $C_{34}H_{35}O_9P$ (618.615): C, 66.02; H, 5.70%. Found:

C, 66.29; H, 5.52%. MS: *m/z* (%) = 618 (M^+, 3), 615 (18), 557 (10), 433 (30), 294 (20), 278 (32), 277 (78), 262 (100), 239 (18), 220 (20), 201 (19), 183 (72), 152(20), 108 (26), 77 (27), 43 (54).

Dimethyl 2-(2,2-dimethyl-4,6-dioxo-5-propionyl-1,3-dioxane-5-yl)-3-(triphenyl-λ^5-phosphanylidene) succinate (6c). IR (KBr) (υ_{max}, cm^{-1}): 1735 (C=O), 1667, 1555 (C=O), 1300, 1264, 1195, 1155 (C−O). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H = 1.24 (3 H, t, *J* 7.1 Hz, CH_3), 1.67 (6 H, t, *J* = 7.2 Hz, 2 CH_3), 1.74 (6 H, s, 2 CH_3), 2.93 (2 H, q, *J* = 7.1 Hz, CH_2), 6.81 (1 H, s, CH), 7.37–7.69 (15 H, m, 3 C_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ_C = 9.6 (CH_2CH_3), 26.8 (2 CH_3), 28.1 (CH), 29.4 (2 CH_2), 42.5 (d, $^1J_{PC}$ = 127.95 Hz, P=C), 52.1 (2 CH_3), 91.6 (C(C=O)$_3$), 104.6 (C(CH_3)$_2$), 122.5 (d, $^1J_{PC}$ = 99.00 Hz, C_{ipso}), 128.2 (d, $^3J_{PC}$ 11.0 Hz, C_{meta}), 130.9 (d, $^4J_{PC}$ 2.0 Hz, C_{para}), 134.5 (d, $^2J_{PC}$ 10.0 Hz, C_{ortho}), 165.1 (d, $^3J_{PC}$ 12.7 Hz, C=O ester), 170.5 (d, $^2J_{PC}$ 13.6 Hz, C=O ester), 194.4 (C=O). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ_P = 29.4 ppm. Anal. calcd. for $C_{33}H_{33}O_9P$ (604.589): C, 65.56; H, 5.50%. Found: C, 65.69; H, 5.42%. MS: *m/z* (%) = 604 (M^+, 3), 530 (6), 443 (8), 420 (10), 347 (15), 293 (15), 278 (30), 277 (70), 262 (100), 201 (20), 183 (73), 152 (18), 108 (23), 77 (25), 57 (30), 43 (45).

Diethyl 2-(2,2-dimethyl-4,6-dioxo-5-propionyl-1,3-dioxane-5-yl)-3-(triphenyl-λ^5-phosphanylidene) succinate (6d). IR (KBr) (υ_{max}, cm^{-1}): 1730, 1666, 1556 (C=O), 1305, 1260, 1189, 1155 (C−O). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H = 1.28 (3H, t, $^3J_{H,H}$ = 7.15 Hz, CH_3), 1.30 (6H, t, $^3J_{H,H}$ = 7.18 Hz, CH_3), 1.74 (6H, s, 2 CH_3), 2.93 (2 H, q, $^3J_{H,H}$ = 7.15 Hz, CH_2), 4.20 (4 H, q, $^3J_{H,H}$ = 7.18 Hz, 2 CH_2), 6.80 (1 H, s, CH), 7.37–7.69 (15 H, m, 3 C_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ_C = 9.6 (CH_2CH_3), 26.7 (2 CH_3), 26.8 (2 OCH_2CH_3), 29.0 (CH), 29.5 (CH_2), 42.8 (d, $^1J_{PC}$ = 128.2 Hz, P=C), 61.3 (2 CH_2), 91.8 (C(C=O)$_3$), 104.8 (C(CH_3)$_2$), 122.9 (d, $^1J_{PC}$ = 99.24 Hz, C_{ipso}), 127.3 (d, $^3J_{PC}$ 11.0 Hz, C_{meta}), 130.5 (d, $^4J_{PC}$ 2.0 Hz, C_{para}), 133.9 (d, $^2J_{PC}$ 10.0 Hz, C_{ortho}), 164.8 (d, $^3J_{PC}$ 12.8 Hz, C=O ester), 170.3 (d, $^2J_{PC}$ 13.8 Hz, C=O ester), 194.5 (C=O). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ_P = 29.1 ppm. Anal. calcd. for $C_{35}H_{37}O_9P$ (632.642): C, 66.45; H, 5.90%. Found: C, 66.29; H, 5.82%. MS: *m/z* (%) = 632 (M^+, 6), 586 (5), 557 (8), 447 (22), 308 (11), 278 (30), 277 (71), 262 (100), 220 (6), 183 (61), 167 (15), 108 (20), 77 (25), 43 (44).

Dimethyl 2-(2,2-dimethyl-4,6-dioxo-5-(2-phenylacetyl)-1,3-dioxane-5-yl)-3-(triphenyl-λ^5-phosphanylidene) succinate (6e). IR (KBr), υ(cm^{-1}): 1735, 1667, 1555 (C=O), 1303, 1264, 1190, 1156 (C−O). Anal. calcd. for $C_{38}H_{35}O_9P$ (666.659): C, 68.46; H, 5.29%. Found: C, 68.29; H, 5.12%. MS: *m/z* (%) = 590 (M^+, 1), 515 (5), 429 (8), 405 (7), 368 (10), 332 (8), 293 (10), 278 (32), 277 (74), 262 (100), 236 (8), 201 (18), 183 (72), 152 (20), 108 (24), 77 (23), 57 (23), 43 (51).

Major: ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H = 1.40 (6H, s, 2CH_3), 3.80 (3H, s, OCH_3), 3.83 (3 H, s, OCH_3), 5.28 (2 H, s, $PhCH_2$), 6.20 (1H, d, J_{PH} = 12.02 Hz, CH), 6.85–8.04 (20 H, m, 4 C_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ_C = 29.7 (C(CH_3)$_2$), 38.1 (PhCH_2), 39.2 (d, $^1J_{PC}$ = 130.07 Hz, P=C), 48.6, 52.1 (2 OCH_3), 61.5 (C(C=O)$_3$), 104.1 (C(CH_3)$_2$), 117.4 (d, $^1J_{PC}$ = 99.02 Hz, C_{ipso}), 125.1–137.7 (4 C_6H_5), 169.1 (d, $^2J_{PC}$ = 14.0 Hz, PC*C*O), 175.6, 209.3 (C=O). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ_P = 23.7 ppm.

Minor: ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H = 1.36 (6H, s, 2CH_3), 3.37 (3H, s, OCH_3), 3.78 (3H, s, OCH_3), 4.95 (2 H, s, $PhCH_2$), 5.92 (1 H, d, J_{PH} 12.08 Hz, CH), 6.85–8.04 (20 H, m, 4 C_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ_C = 29.2 (C(CH_3)$_2$), 38.2 (PhCH_2), 45.9 (d, $^1J_{PC}$ = 130.02 Hz, P=C), 48.6, 57.2 (2 OCH_3), 62.6 (C(C=O)$_3$), 104.3 (C(CH_3)$_2$), 120.4 (d, $^1J_{PC}$ = 99.02 Hz, C_{ipso}), 125.1–137.7 (4 C_6H_5), 172.1 (d, $^2J_{PC}$ = 14.0 Hz, PC*C*O), 175.8 (C=O), 210.3 (C=O). ^{31}P NMR (121.49 MHz, $CDCl_3$): δ_P = 23.1 ppm.

Diethyl 2-(2,2-dimethyl-4,6-dioxo-5-(2-phenylacetyl)-1,3-dioxane-5-yl)-3-(triphenyl-λ^5-phosphanylidene) succinate (6f). IR (KBr), υ(cm^{-1}): 1722, 1662, 1587 (C=O), 130, 1259, 1195, 1199 (C−O). Anal. calcd. for $C_{38}H_{35}O_9P$ (694.713): C, 69.16; H, 5.66%. Found: C, 68.98; H, 5.62%. MS: *m/z* (%) = 590 (M^+, 1), 515 (5), 429 (8), 405 (7), 368 (10), 332 (8), 293 (10), 278 (32), 277 (74), 262 (100), 236 (8), 201 (18), 183 (72), 152(20), 108 (24), 77 (23), 57 (23), 43 (51).

Major: ^{1}H NMR (300.1 MHz, $CDCl_3$): $\delta_H = 0.48$ (3 H, t, $^3J_{H,H} = 7.16$ Hz, CH_2CH_3), 1.49 (3 H, t, $^3J_{H,H} = 7.16$ Hz, CH_2CH_3), 1.36 (6 H, s, $C(CH_3)_2$), 4.11 (2 H, q, $^3J_{H,H} = 7.16$ Hz, OCH_2), 4.25 (2 H, q, $^3J_{H,H} = 7.16$ Hz, OCH_2), 5.27 (2 H, s, $PhCH_2$), 6.15 (1H, d, $J_{PH} = 12.60$ Hz, CH), 6.83–8.00 (20 H, m, 4 C_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta_C = 13.4$ (CH_2CH_3), 14.0 (CH_2CH_3), 27.7 (CH), 29.9 ($C(CH_3)_2$), 38.0 ($PhCH_2$), 40.0 (d, $^1J_{PC} = 130.07$ Hz, P=C), 48.6, 58.8 (OCH_2), 60.8 (OCH_2), 63.1 ($C(C=O)_3$), 104.1 ($C(CH_3)_2$), 118.5–137.9 (4 C_6H_5), 168.7 (d, $^2J_{PC} = 12.75$ Hz, PC*C*O), 175.3, 209.6 (C=O). ^{31}P NMR (121.49 MHz, $CDCl_3$): $\delta_P = 23.9$ ppm.

Minor: ^{1}H NMR (300.1 MHz, $CDCl_3$): $\delta_H = 0.30$ (3H, t, $^3J_{H,H} = 7.15$ Hz, CH_2CH_3), 1.29 (3H, t, $^3J_{H,H} = 7.16$ Hz, CH_2CH_3), 1.30 (6 H, s, $C(CH_3)_2$), 3.50 (2 H, q, $^3J_{H,H} = 7.15$ Hz,OCH_2), 3.70 (2 H, q, $^3J_{H,H} = 7.15$ Hz,OCH_2), 5.30 (2 H, s, $PhCH_2$), 5.80 (1 H, d, $J_{PH} = 12.65$ Hz, CH), 6.83–8.00 (20 H, m, 4 C_6H_5). ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta_C = 12.9$ (CH_2CH_3), 15.3 (CH_2CH_3), 28.1 (CH), 29.8 ($C(CH_3)_2$), 38.0 ($PhCH_2$), 44.5 (d, $^1J_{PC} = 130.07$ Hz, P=C), 48.6, 57.1 (OCH_2), 58.9 (OCH_2), 63.1 ($C(C=O)_3$), 104.1 ($C(CH_3)_2$), 118.5–137.9 (4 C_6H_5), 168.7 (d, $^2J_{PC} = 12.75$ Hz, PC*C*O), 175.3, 208.9 (C=O). ^{31}P NMR (121.49 MHz, $CDCl_3$): $\delta_P = 23.9$ ppm.

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