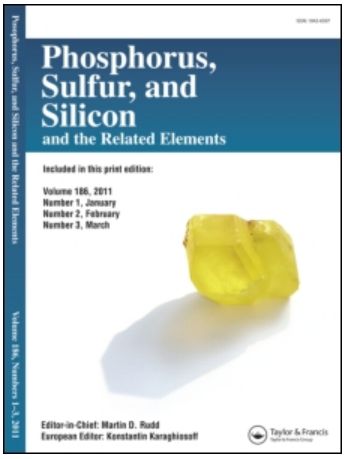

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SYNTHESIS OF DIALKYL 2-(1-CYANO-2-OXO-1-PHENYL-ALKYL)-3-(TRIPHENYL-λ⁵-PHOSPHANYLIDENE)-SUCCINATES

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SYNTHESIS OF DIALKYL 2-(1-CYANO-2-OXO-1-PHENYL-ALKYL)-3-(TRIPHENYL-λ^5-PHOSPHANYLIDENE)-SUCCINATES

Issa Yavari,[a] *Mohammad R. Islami,*[b] *Azizollah Habibi,*[a] *Ahmad M. Tikdari,*[b] *and Lona Ebrahimi*[b]
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3-Oxo-2-phenyl-butanenitrile or 3-oxo-2-phenyl-pentanenitrile undergo a smooth reaction with dialkyl acetylenedicarboxylates in the presence of triphenylphosphine to produce highly-functionalized salt-free ylides in nearly quantitative 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 resulting from conjugation of the ylide moiety with the adjacent carbonyl group.

Keywords: Acetylenic esters; CH-acid; rotational isomers; stable phosphorus ylides; triphenylphosphine

Phosphorus ylides are reactive intermediates and have important application in chemical, biological, and industrial synthetic uses.[1–6] These ylides are usually prepared by treatment of phosphonium salts with a base. We report on the reaction between dialkyl acetylenedicarboxylates **1** and 3-oxo-2-phenyl-butanenitrile (**2a**) or 3-oxo-2-phenyl-pentanenitrile (**2b**) and in the presence of triphenylphosphine. Thus, reaction of these keto-nitriles with the electron-defficient acetylenic esters **1** leads to stable phosphorus ylides **3** in good yields (see Scheme 1).

RESULTS AND DISCUSSION

The reaction of dialkyl acetylenedicarboxylates **1** with keto-nitriles **2** in the presence of triphenylphosphine proceeded smoothly at room

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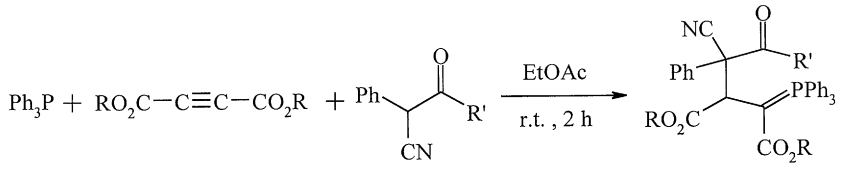


1	R
a	Me
b	Et
c	*iso*-Pr

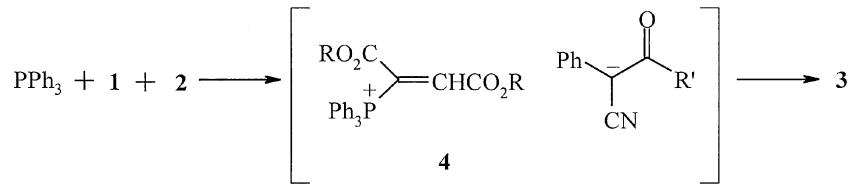
2	R'
a	Me
b	Et

3	R	R'
a	Me	Me
b	Et	Me
c	Me	Et
d	Et	Et
e	*iso*-Pr	Et

SCHEME 1

temperature in ethyl acetate and was completed within a few hours. ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of phosphorane **3**. Any product other than **3** could not be detected by NMR spectroscopy. The structures of compounds **3a–e** were deduced from their elemental analyses and IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra.

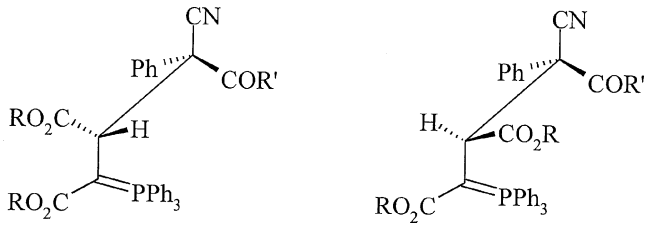
On the basis of the well established chemistry of trivalent of phosphorus nucleophiles,[1–9] it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester **1** and subsequent protonation of the 1:1 adduct by the C–H acid **2** to form phosphorane **3** (see Scheme 2).



SCHEME 2

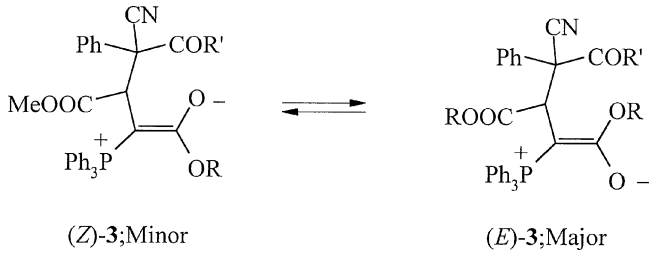
Compound **3** has two stereogenic centers, and therefore two diastereomers are expected (Scheme 3). However, the ^{1}H NMR spectra of the crude reaction mixtures were consistent with the presence of only one diastereomer (see Experimental).

^{1}H, ^{13}C, and ^{31}P NMR spectra of the ylides **3a–3e** are consistent with the presence of two rotamers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in the (*E*)-**3** and (*Z*)-**3** geometrical isomers



SCHEME 3

(Scheme 4) is slow on the NMR time scale at ambient temperature. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **3a–3e** are shown in Table I. Assignment of configuration (*Z*) to the minor geometrical isomer is based on the ^{1}H chemical shift of the OR moiety, which is expected to be shielded as a result of the anisotropic effect of the phenyl groups (see Scheme 4).

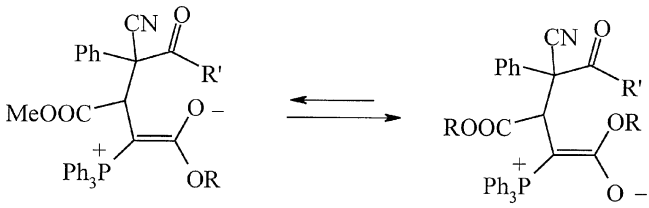


SCHEME 4

The methoxy region of the ^{1}H NMR spectrum of **3a** in $CDCl_3$ at ambient temperature (25°C) exhibits two sharp singlets for the CO_2CH_3 groups of (*E*) and (*Z*) isomers and two fairly broad singlets for the OCH_3 groups. Near 10°C the broad lines become sharper. The ^{1}H NMR of **3a** in 1,2-dichlorobenzene at 10°C is similar to that measured in $CDCl_3$ (Table II). Increasing the temperature results in coalescence of the OCH_3 resonances. At 100°C, a relatively broad singlet was observed for the OCH_3 group, while the CO_2CH_3 protons appear as a sharp single resonance.

Although an extensive line-shape analysis in relation to the dynamic ^{1}H NMR effect observed for **3a** was not undertaken, the variable

TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-3, CO_2R, OR, C-2, and C-3 in the Major (M) and Minor (m) Geometrical Isomers of **3a–3e**



(*Z*)-**3**;Minor (*E*)-**3**;Major

SCHEME 2

		^{1}H NMR data			^{13}C NMR data		
Comp.	Isomer (%)	H-2 ($^{3}J_{PH}$)	OR	CO_2R	C-2($^{2}J_{PC}$)	C-3($^{1}J_{PC}$)	^{31}P
3a	M (75)	3.96 (19)	3.64	3.77	50.99 (14)	38.74 (136)	24.02
3a	m (25)	3.82 (15)	2.99	3.64	51.90 (13)	37.26 (127)	24.15
3b	M (64)	3.88 (20)	3.95[a]	4.30[a]	52.16 (13)	38.74 (136)	23.67
3b	m (36)	3.79 (19)	3.52[a]	4.23[a]	51.25 (13)	36.96 (127)	23.74
3c	M (60)	3.96 (19)	3.63	3.77	52.27 (10)	38.70 (136)	23.80
3c	m (40)	3.82 (15)	2.99	3.79	51.25 (13)	37.12 (126)	23.30
3d	M (62)	3.90 (20)	3.95[a]	4.23[a]	52.43 (10)	38.80 (136)	23.89
3d	m (38)	3.84 (15)	3.52[a]	3.74[a]	51.63 (10)	37.00 (128)	23.75
3e	M (55)	3.83 (20)	4.74[b]	5.10[b]	52.66 (14)	39.62 (136)	23.50
3e	m (45)	3.81 (20)	4.91[b]	5.17[b]	51.26 (14)	36.80 (127)	23.87

[a]The methylene group of the OR moiety.
[b]The methine group of the OR moiety.

temperature spectra allowed to calculate the free energy barrier (but not the enthalpy and entropy of activation) for the dynamic NMR process in **3a**. From coalesence temperature of the methoxy proton resonances and using the expression, $k = \pi \Delta v / \sqrt{2}$, we calculate[10] that

TABLE II Selected Proton Chemical Shifts (at 500.1 MHz, TMS) and Activation Parameters for **3a** in 1,2-Dichlorobenzene

		Resonance (P–C–CO_2CH_3)					
Comp.	Temp/°C	ppm		Δv/Hz	k/s^{-1}	Tc/K	$\Delta G^{\neq}$/kJ mol^{-1}
3a	10	2.99	3.63	320	710	353	103.3 ± 2
3a	80	3.46					

the first-order rate constant (k) for the dynamic NMR effect in **3a** is 710 s^{-1} at 353 K. Application of the absolute rate theory with a transmission coefficient of **1** gives a free-energy of activation ($\Delta G^{\neq}$) of 103.3 ± 2 kJ mol^{-1} (Table II), where all known sources of errors are estimated and included. The experimental data available are not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, even though the errors in $\Delta G^{\neq}$ are not large.[11]

In conclusion, the present method features the advantages that the reaction can be performed under neutral conditions and the starting materials and reagents can be mixed without any activation or modification. Phosphorus ylides **3a–3e** can be considered as potentially useful synthetic intermediates. The procedure described here provides an acceptable method for the preparation of phosphoranes bearing a ketonitrile residue.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. IR spectra were recorded as KBr discs on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded at 500.1, 125.8, and 202.4 MHz, respectively, on a Bruker DRX 500-AVANCE FT-NMR instrument with $CDCl_3$ as solvent and TMS as internal standard. Reagents were obtained from Fluka (Buchs, Switzerland) and used without further purification.

Preparation of Dimethyl 2-(Cyano-2-oxo-1-phenyl-propyl)-3-(triphenyl-λ^5-phosphanylidene)-succinate 3a

General Procedure

To a magnetically stirred solution of 0.52 g triphenylphosphine (2 mmol) and 0.32 g 3-oxo-2-phenyl-butanenitrile (2 mmol) in 15 mL of ethyl acetate was dropwise added a mixture of 0.28 g dimethyl acetylenedicarboxylate (2 mmol) in 5 mL of ethyl acetate at room temperature over 10 min. After 12 h stirring the product was filtered off and recrystallized from ethyl acetate. Colorless crystals m.p. 163–165°C, yield 1.0 g, 90%, IR (KBr) (ν_{max}, cm^{-1}): 2250 (CN), 1740 and 1655 (C=O). Anal. Calcd for $C_{34}H_{30}NO_5P$ (563.6): C, 75.50; H, 5.35; N, 2.49%; Found: C, 75.2; H, 5.3; N, 2.4%.

Major isomer (*E*)-**3a** (75%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.36 (3 H, s, CH_3), 3.64 and 3.77 (6 H, 2 s, 2 OCH_3), 3.96 (1 H, d, $^{3}J_{PH} = 19.$ Hz, CH), 7.0–7.69 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 27.47

(CH_3), 38.74 (d, $^1J_{PC} = 136$ Hz, P═C), 49.27 and 52.24 (2 OCH_3), 50.99 (d, $^2J_{PC} = 14$ Hz, CH), 62.60 (*C*CN), 120.76 (CN), 128.60 (d, $^1J_{PC} = 90$ Hz, P─C), 129.24 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.50 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.75 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 165.20 (d, $^2J_{PC} = 19$ Hz, P─C═*C*), 174.32 (d, $^2J_{PC} = 19$ Hz, C═O), 201.00 (C═O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.02 (Ph_3P^+─C).

Minor isomer (*Z*)-**3a** (25%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.38 (3 H, s, $^3J_{HH} = 6.9$ Hz, CH_3), 2.99 and 3.79 (6 H, 2 s, 2 OCH_3), 3.82 (1 H, d, $^3J_{PH} = 15$ Hz, CH), 7.0–7.69 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 27.47 (CH_3), 37.26 (d, $^1J_{PC} = 127$ Hz, P─C), 48.82 and 52.20 (2 OCH_3), 51.90 (d, $^2J_{PC} = 13$ Hz, CH), 62.19 (*C*CN), 120.76 (CN), 128.40 (d, $^1J_{PC} = 90$ Hz, P─C), 129.24 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.50 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.75 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 169.39 (d, $^2J_{PC} = 19$ Hz, P─C═*C*), 170.87 (d, $^2J_{PC} = 19$ Hz, C═O), 203.44 (C═O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 24.15 (Ph_3P^+─C).

Diethyl 2-(Cyano-2-oxo-1-phenyl-propyl)-3-(triphenyl-λ^5-phosphanylidene)-succinate 3b

Colorless crystals m.p. 133–136°C, yield 1.10 g, 93%. IR (KBr) (ν_{max}, cm^{-1}): 2250 (CN), 1720 and 1650 (C═O). Anal. Calcd for $C_{36}H_{34}NO_5P$ (591.7): C, 73.10; H, 5.79; N, 2.37%; Found: C, 72.9; H, 5.7; N, 2.3%.

Major isomer (*E*)-**3b** (64%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.33 (3 H, t, $CH_2C\mathit{H}_3$), 2.38 (3 H, s, $C\mathit{H}_3$), 3.88 (1 H, d, $^3J_{PH} = 20$ Hz, CH), 3.95 and 4.30 (6 H, 2 ABX_3 system, 2 $OC\mathit{H}_2C\mathit{H}_3$), 7.0–7.69 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.29 (CH_2CH_3), 27.47 (CH_3), 38.74 (1 H, d, $^1J_{PC} = 136$ Hz, P─C), 49.27 and 52.24 (2 OCH_3), 52.16 (d, $^2J_{PC} = 13$ Hz, CH), 62.60 (*C*CN), 120.89 (CN), 128.62 (d, $^1J_{PC} = 90$ Hz, P─C), 129.20 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.50 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.84 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 165.20 (d, $^2J_{PC} = 19$ Hz, P─C═*C*), 174.56 (d, $^2J_{PC} = 19$ Hz, C═O), 200.41 (C═O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.67 (Ph_3P^+─C).

Minor isomer (*Z*)-**3b** (36%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.28 (3 H, t, $^3J_{HH} = 6.9$ Hz, CH_3), 2.38 (3 H, s, CH_3), 3.52 and 4.23 (6 H, 2 ABX_3 system, 2 $OC\mathit{H}_2CH_3$), 3.79 (1 H, d, $^3J_{PH} = 19$ Hz, CH), 7.0–7.69 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 15.00 (CH_2CH_3), 27.47 (CH_3), 36.96 (d, $^1J_{PC} = 127$ Hz, P─C), 48.82 and 52.16 (2 OCH_3), 51.15 (d, $^2J_{PC} = 13$ Hz, CH), 62.19 (*C*CN), 120.89 (CN), 128.30 (d, $^1J_{PC} = 90$ Hz, P─C), 129.20 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.50 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.84 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 169.39 (d, $^2J_{PC} = 19$ Hz, P─C═*C*), 170.87 (d, $^2J_{PC} = 19$ Hz, C═O), 203.61 (C═O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.74 (Ph_3P^+─C).

Dimethyl 2-(Cyano-2-oxo-1-phenyl-butyl)-3-(triphenyl-λ^5-phosphanylidene)-succinate 3c

Colorless crystals m.p. 165–168°C, yield 1.0 g, 88%. IR (KBr) (ν_{max}, cm^{-1}): 2250 (CN), 1725 and 1640 (C=O). Anal. Calcd for $C_{35}H_{32}NO_5P$ (577.6): C, 72.78; H, 5.58; N, 2.43%; Found: C, 72.5; H, 5.5; N, 2.4%.

Major isomer (*E*)-**3c** (60%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.90 (3 H, t, $^3J_{HH} = 6.9$ Hz, CH_2*Me*), 2.49 (2 H, ABX_3 system, C*H*$_2$Me), 3.63 and 3.77 (6 H, 2 s, 2 OMe), 3.96 (1 H, d, $^3J_{PH} = 19$ Hz, CH), 6.98–7.51 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 8.07 (CH_2Me), 33.14 (*C*H$_2$Me), 38.70 (d, $^1J_{PC} = 136$ Hz, P–C), 49.12 and 49.85 (2 OMe), 52.27 (d, $^2J_{PC} = 10$ Hz, CH), 62.43 (*C*CN), 120.74 (CN), 128.40 (d, $^1J_{PC} = 90$ Hz, P–C), 129.54 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.15 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.81 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 169.48 (d, $^2J_{PC} = 19$ Hz, P–C=*C*), 174.51 (d, $^2J_{PC} = 19$ Hz, C=O), 203.51 (C=O). ^{31}P NMR (202.4 MHz, $CDCl_3$) δ 23.80 (Ph_3P^+–C).

Minor isomer (*Z*)-**3c** (40%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.93 (3 H, t, $^3J_{HH} = 6.9$ Hz, CH_2*Me*), 2.49 (2 H, ABX_3 system, C*H*$_2$Me), 2.99 and 3.79 (6 H, 2 s, 2 OMe), 3.82 (1 H, d, $^3J_{PH} = 15$ Hz, CH), 6.98–7.51 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 8.12 (CH_2*Me*), 33.14 (*C*H$_2$*Me*), 37.12 (d, $^1J_{PC} = 126$ Hz, P–C), 48.20 and 48.85 (2 OMe), 51.25 (d, $^2J_{PC} = 13$ Hz, CH), 61.99 (*C*CN), 120.74 (CN), 128.40 (d, $^1J_{PC} = 90$ Hz, P–C), 129.54 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.15 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.81 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 165.48 (d, $^2J_{PC} = 19$ Hz, P–C=*C*), 170.44 (d, $^2J_{PC} = 19$ Hz, C=O), 203.40 (C=O). ^{31}P NMR (202.4 MHz. $CDCl_3$) δ 23.30 (Ph_3P^+–C).

Diethyl 2-(Cyano-2-oxo-1-phenyl-butyl)-3-(triphenyl-λ^5-phosphanylidene)-succinate 3d

Colorless crystals m.p. 158–160°C, yield 1.10 g, 88%. IR (KBr) (ν_{max}, cm^{-1}): 2250 (CN), 1720 and 1635 (C=O). Anal. Calcd for $C_{37}H_{36}NO_5P$ (605.6): C, 73.38; H, 5.99; N, 2.31%; Found: C, 73.3; H, 5.9; N, 2.3%.

Major isomer (*E*)-**3d** (62%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.90 (3 H, t, $^3J_{HH} = 7.0$ Hz, CH_2*Me*), 1.24 (3 H, t, $^3J_{HH} = 7.0$ Hz, CH_2*Me*) 3.24 (2 H, ABX_3 system, C*H*$_2$Me), 3.90 (1 H, d, $^3J_{PH} = 20$ Hz, CH), 3.95 and 4.23 (4 H, s, *OCH*$_2$Me), 7.0–7.9 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 7.98 (CH_2*Me*), 14.29 and 15.06 (2 OCH_2*Me*), 33.00 (*C*H$_2$Me), 38.80 (d, $^1J_{PC} = 136$ Hz, P–C), 52.43 (d, $^2J_{PC} = 10$ Hz, CH), 57.95 and 61.41 (2 *OCH*$_2$Me), 62.43 (*C*CN), 120.79 (CN), 128.23 (d, $^1J_{PC} = 90$ Hz, P–C), 128.86 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 133.27 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.82 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 169.04 (d, $^2J_{PC} = 14.24$ Hz, P–C=*C*),

174.00 (d, $^2J_{PC} = 25.5$ Hz, C═O), 203.29 (C═O). ^{31}P NMR (202.4 MHz. $CDCl_3$) δ 23.89 (Ph_3P^+–C).

Minor isomer (*Z*)-**3d** (38%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.34 (3 H, t, $^3J_{HH} = 6.9$ Hz, CH_2*Me*), 1.35 (3 H, t, CH_2*Me*), 2.52 (2 H, ABX_3 system, *C*H_2Me), 3.52 and 3.74 (4 H, 2 q, 2 OCH_2), 3.84 (1H, d, $^3J_{PH} = 15$ Hz, CH), 7.0–7.9 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 8.05 (CH_2*Me*), 13.77 and 15.80 (2 OCH_2*Me*), 33.0 (*C*H_2Me), 37.00 (d, $^1J_{PC} = 128.2$ Hz, P–C), 51.63 (d, $^2J_{PC} = 10$ Hz, CH), 57.60 and 61.35 (2 OCH_2), 62.12 (*C*CN), 120.90 (CN), 128.23 (d, $^1J_{PC} = 90$ Hz, P–C), 128.86 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 133.27 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.82 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 166.10 (d, $^2J_{PC} = 18$ Hz, P–C═*C*), 170.73 (d, $^2J_{PC} = 18$ Hz, C═O), 203.29 (C═O). ^{31}P NMR (202.4 MHz. $CDCl_3$) δ 23.75 (Ph_3P^+–C).

Diisopropyl 2-(Cyano-2-oxo-1-phenyl-butyl)-3-(triphenyl-λ^5-phosphanylidene)-succinate 3e

Colorless crystals m.p. 148–150°C, yield 1.12 g, 88%. IR (KBr) (ν_{max}, cm^{-1}): 2250 (CN), 1728 and 1685 (C═O). Anal. Calcd for $C_{39}H_{40}NO_5P$ (633.7): C, 73.92; H, 6.36; N, 2.21%; Found: C, 73.5; H, 6.3; N, 2.1%.

Major isomer (*E*)-**3e** (55%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.42, 0.89, 1.25 and 1.29 (12 H, 4d, $^3J_{HH} = 6.9$ Hz, 2 CH*Me*$_2$), 1.40 (3H, t, $^3J_{HH} = 6.9$ Hz, CH_2*Me*), 2.51 (2 H, ABX_3 system, *C*H_2Me), 3.83 (1 H, d, $^3J_{PH} = 20$ Hz, CH), 4.74 and 5.10 (2 H, 2 m, 2 OCH), 7.04–7.89 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 8.0 (CH_2*Me*), 21.35, 21.86, 21.99, and 22.13 (2 CH*Me*$_2$), 33.12 (*C*H_2Me), 36.62 (d, $^1J_{PC} = 136$ Hz, P–C), 52.66 (d, $^2J_{PC} = 14$ Hz, CH), 62.14 (*C*CN), 64.47, and 68.90 (2 OCH), 121.00 (CN), 127.45 (d, $^1J_{PC} = 90$ Hz, P–C), 129.20 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.55 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.88 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 168.30 (d, $^2J_{PC} = 13$ Hz, P–C═*C*), 173.26 (d, $^2J_{PC} = 19$ Hz, C═O), 203.50 (C═O). ^{31}P NMR (202.4 MHz. $CDCl_3$) δ 23.80 (Ph_3P^+–C).

Minor isomer (*Z*)-**3e** (45%), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.54, 0.91, 1.25, and 1.35 (12 H, 4 d, $^3J_{HH} = 6.7$ Hz, 2 CH*Me*$_2$), 1.26 (3 H, t, $^3J_{HH} = 6.9$ Hz, CH_2*Me*), 3.25 (2 H, ABX_3 system, *C*H_2Me), 3.81 (1 H, d, $^3J_{PH} = 20$ Hz, CH), 4.91 and 5.17 (2 H, 2 m, 2 OCH), 7.04–7.89 (20 H, m, 4 C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 8.00 (CH_2*Me*), 21.73, 21.99, 22.13, and 22.75 (2 CH*Me*$_2$), 33.12 (*C*H_2Me), 36.80 (d, $^1J_{PC} = 136$ Hz, P–C), 51.26 (d, $^2J_{PC} = 14$ Hz, CH), 61.90 (*C*CN), 66.42, and 69.00 (2 OCH), 121.28 (CN), 127.45 (d, $^1J_{PC} = 90$ Hz, P–C), 129.20 (d, $^3J_{PC} = 12$ Hz, C_{meta}), 132.55 (d, $^4J_{PC} = 2$ Hz, C_{para}), 133.88 (d, $^3J_{PC} = 10$ Hz, C_{ortho}), 164.50 (d, $^2J_{PC} = 19$ Hz, P–C═*C*), 170.40 (d, $^2J_{PC} = 13$ Hz, C═O), 203.26 (C═O). ^{31}P NMR (202.4 MHz. $CDCl_3$) δ 23.87 (Ph_3P^+–C).

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