# A simple synthesis of stable phosphorus ylides containing cyano groups, from the reaction between triphenylphosphine and acetylenic esters in the presence of CH- acid compounds

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**Abstract**

Stable crystalline phosphorus ylides were obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylenedicarboxylates, in the presence of strong CH- acids such as malononitrile or ethyl cyanoacetate. These stable ylides exist in solution 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.

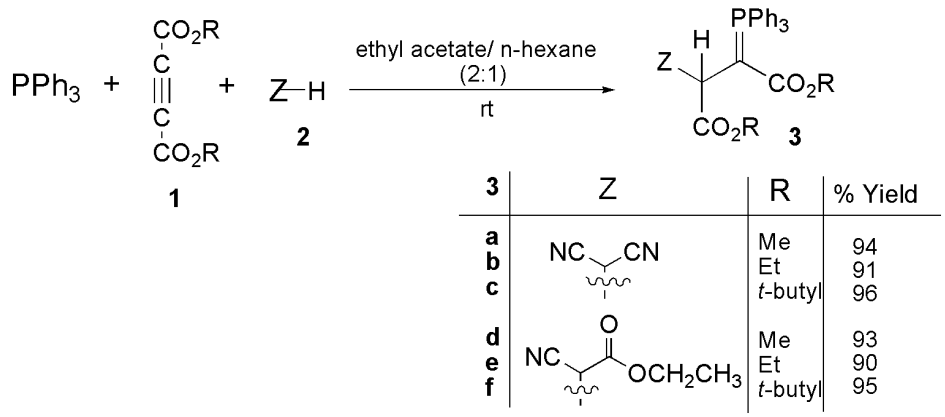
**Keywords:** Acetylenic ester, CH- acids, stable phosphorus ylides, triphenylphosphine, geometrical isomer

## Introduction

The synthesis of phosphorus ylides is important in organic chemistry because of their applications in the synthesis of organic products,[1] especially the synthesis of naturally-occurring products with potentially useful biological and pharmacological properties.[2] Phosphorus ylides are reactive intermediates, which take part in many valuable reactions in organic synthesis,[3–5] and several methods have been developed for their preparation. These ylides are usually prepared by treatment of a phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and an alkyl halide.[1,6–10] Among other methods, phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins.[6–21] We report here an efficient synthetic route for the generation of stable phosphoranes bearing cyano groups *via* the reaction of triphenylphosphine with dialkyl acetylenedicarboxylates (**1**) in the presence of

strong CH-acids such as malononitrile or ethyl cyanoacetate (**2**), which leads to the corresponding stable phosphorus ylides (**3**) in excellent yields (Scheme 1).



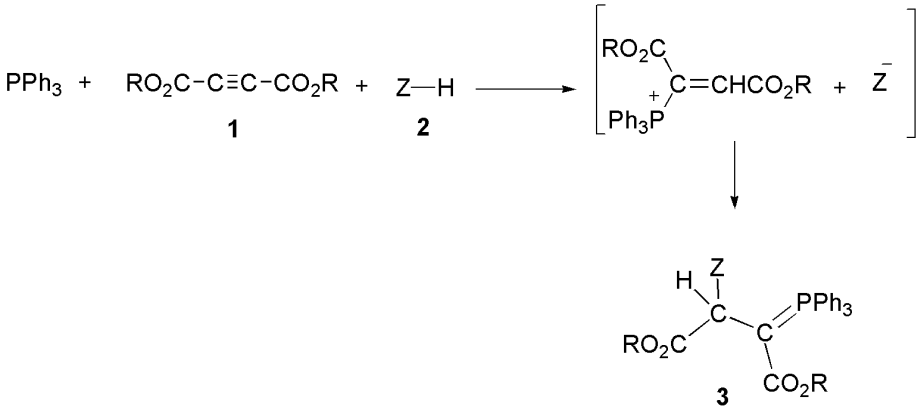

| 3 | Z | R | % Yield |
|---|---|---|---|
| a | NC, CN | Me | 94 |
| b | | Et | 91 |
| c | | *t*-butyl | 96 |
| d | NC, O, $OCH_2CH_3$ | Me | 93 |
| e | | Et | 90 |
| f | | *t*-butyl | 95 |

**Scheme 1**

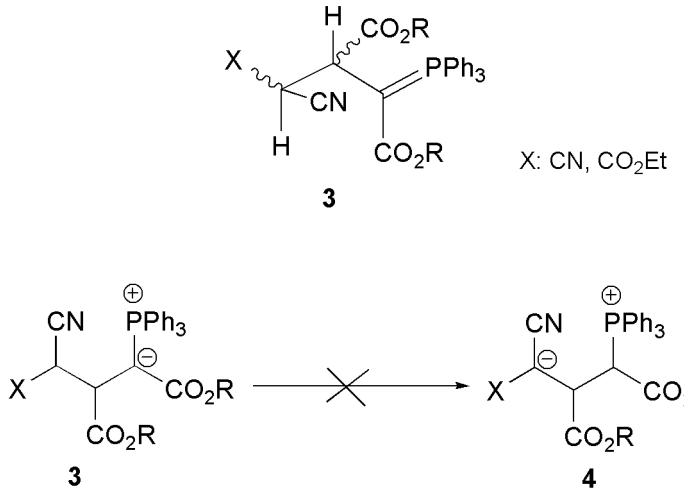
## Result and Discussion

The reactions of malononitrile or ethyl cyanoacetate (**2**) with dialkyl acetylenedicarboxylates (**1**) in the presence of triphenylphosphine proceeded in a mixture of ethyl acetate and *n*-hexane (2:1) at room temperature and were complete within 1 hour. The $^{1}$H- and $^{13}$C- NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides, **3**. No products other than **3** could be detected by NMR spectroscopy. The structures of compounds **3a–f** were deduced from their IR-, $^{1}$H-, $^{13}$C- and $^{31}$P- NMR spectra. The mass spectra of the products displayed molecular ion peaks at appropriate *m/z* values. Any initial fragmentations involved the loss of alkoxy, alkoxycarbonyl, and $PPh_3$ moieties.

The $^{1}$H-**,** $^{13}$C-**,** and $^{31}$P- NMR spectra of ylides **3a–f** are consistent with the presence of two geometrical isomers. The ylide moiety of these compounds is conjugated with the adjacent carbonyl group, and rotation around the partial double bond of the (*E*)- **3** and (*Z*)- **3** geometrical isomers is slow on the NMR timescale 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**–**f** are shown in Table 1. On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[1,6,7] it is reasonable to assume that the phosphorus ylides (**3**) result from the initial addition of triphenylphosphine to the acetylenic ester and subsequent deprotonation of the 1:1 adduct (Scheme 2).



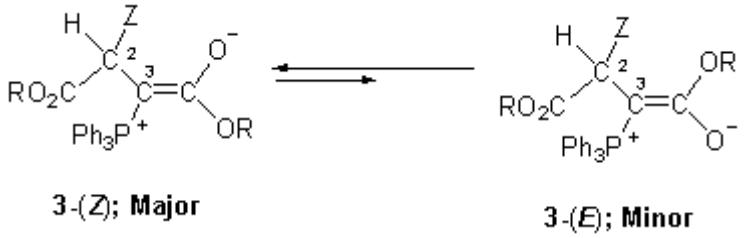

**Scheme 2**




**Scheme 3**

The $^{1}$H- NMR spectra of compounds **3** verified that compound **4** had not been formed under these conditions, and the *anti*- conformation of the two vicinal protons in compounds **3** was supported by the value of $^{3}J_{HH}$: partial assignments are given in the Experimental Section (see Scheme 3 and 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, -OR, -$CO_2$R, C-2, and C-3, in the Major (M) and Minor (m) diastereoisomers of compounds **3a**–**f**.




| Compd | Isomer (%) | $^{1}$H NMR data | | | $^{13}$C NMR data | | |
|---|---|---|---|---|---|---|---|
| | | H-2 ($^{3}J_{PH}$) | OR | $CO_2$R | C-2 ($^{2}J_{PC}$) | C-3 ($^{1}J_{PC}$) | $^{31}$P NMR |
| **3a** | M (74) | 2.90 (16.0) | 3.17 | 3.77 | 46.88 (14.5) | 39.66 (128.8) | 22.90 |
| **3a** | m (26) | 2.95 (15.6) | 3.58 | 3.76 | 46.20 (14.2) | 40.75 (137.3) | 23.60 |
| **3b** | M (75) | 2.88 (16.1) | 3.71 | 4.25 | 46.92 (15.1) | 39.56 (129.1) | 22.80 |
| **3b** | m (25) | 2.94 (17.7) | 4.13 | 4.31 | 46.39 (14.2) | 40.83 (137.4) | 23.61 |
| **3c** | M (79) | 2.74 (16.2) | 0.95 | 1.50 | 47.83 (15.1) | 39.54 (129.8) | 22.40 |
| **3c** | m (21) | 2.71 (16.3) | 1.45 | 1.47 | 46.93 (14.7) | 41.31 (137.5) | 23.87 |
| **3d** | M (64) | 3.05 (16.6) | 3.14 | 3.65 | 44.37 (14.4) | 39.39 (128.3) | 23.20 |
| **3d** | m (36) | 3.10 (16.5) | 3.56 | 3.64 | 43.62 (14.5) | 40.31 (136.9) | 23.57 |
| **3e** | M (67) | 3.05 (16.5) | 3.05–3.11 | 4.00-4.20 | 44.47 (14.5) | 39.27 (128.5) | 23.19 |
| **3e** | m (33) | 3.11 (16.6) | 3.71–3.78 | 4.00-4.20 | 43.84 (14.3) | 40.44 (136.9) | 23.73 |
| **3f** | M (70) | 2.84 (18.7) | 0.95 | 1.43 | 45.37 (14.8) | 39.07 (129.1) | 22.56 |
| **3f** | m (30) | 2.91 (17.1) | 1.41 | 1.45 | 44.28 (14.7) | 41.01 (136.3) | 22.40 |

The assignment of **3**-(*E*)- and **3**-(*Z*)- rotamers as the major and minor components in phosphorus ylides have been reported previously in the literature.[22–24] The $^{1}$H- NMR spectrum of compound **3a** exhibits two sharp lines (δ 3.17 and 3.77) arising from the methoxy group in the *Z*-rotamer and two single sharp resonances at 3.58 and 3.76 ppm for methoxy groups in the *E*-rotamer. The shift at 3.21 of the methoxy group of the *Z*- rotamer is shielded, due to the anisotropic effect of the phenyl groups of triphenylphosphine. This effect confirms why the **3**-*E* and **3**-*Z* rotamers could appear as the minor and major forms, respectively, as reported in the Experimental Section. Also, the signals for methine protons at δ 2.90, 2.95, 4.91 and 5.46 ppm, appear as two doublets of doublets ($^{3}J_{PH}$=16 and $^{3}J_{HH}$=10.5 Hz) and ($^{3}J_{PH}$=15.6 and $^{3}J_{HH}$=10.5 Hz) and two doublets ($^{3}J_{HH}$=10.5 and $^{3}J_{HH}$=10.5 Hz) for the major and minor geometrical isomers, respectively. The $^{13}$C- NMR spectrum of **3a** exhibits 26 distinct resonances, which are in agreement with the mixture of two conformational isomers. Although the presence of the $^{31}$P nucleus complicated both the $^{1}$H- and $^{13}$C- NMR spectra of phosphorane **3a**, it helps in assigning the signals by long-range spin–spin couplings with the $^{1}$H- and $^{13}$C- nuclei. The $^{1}$H- and $^{13}$C-NMR spectra of compounds **3b–c** are similar to those of **3a**, except for the signals from the ester group, which appear as characteristic resonance lines with the corresponding chemical shifts. The structural assignments made for phosphoranes **3a–f** on the basis of the $^{1}$H- and $^{13}$C- NMR spectra were supported by their IR spectra. Of special interest is the absorption of the ester groups of such compounds at 1742–1614 cm$^{-1}$. The conjugation of one ester group with the negative charge is a plausible factor in the decrease in the wavenumbers of the corresponding carbonyl absorption bands.

In summary, we have prepared novel stable cyano-functional phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong CH-acids such as malononitrile or ethyl cyanoacetate. The present method has the advantage that not only is the reaction performed under neutral conditions, but also that the reagents can be mixed without any activation or modification.

## Experimental Section

**General Procedures.** Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer respectively. The $^{1}$H-, $^{13}$C-, and $^{31}$P- NMR spectra were obtained from a BRUKER DRX-300 AVANCE instrument with $CDCl_3$ as a solvent at 300.1, 75.5, and 121.5 MHz, respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Mass spectra were recorded on Shimadzu GCMS-QP5050A and Finnigan-MAT 8430 mass spectrometers operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates, triphenylphosphine, malononitrile, and ethyl cyanoacetate were purchased from Fluka (Buchs) and used without further purification. RT denotes room temperature.

**General preparative procedure, exemplified by dimethyl 2-(dicyanomethyl)-3-(triphenylphosphanylidene)butanedioate** (**3a**)

To a magnetically stirred solution of malononitrile (0.06 g , 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in a mixture of ethyl acetate and *n*-hexane (2:1, v/v) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.12 mL, 1 mmol) in 3 mL of ethyl acetate at –5 °C over 10 min. After approximately 1 hour stirring at RT the product was filtered off and washed with cold diethyl ether (3 ×5 mL), and was finally obtained as a white powder, 0.44 g, yield 94%, mp 182–185 °C, IR (KBr) ($\nu_{max}$, cm$^{-1}$): 2225 (CN), 1735 and 1618 (C=O). MS (*m/z*, %): 406 (30), 405 (100), 262 (8), 183 (27), 108 (15), 77 (13), 59 (8). Anal. Calcd for $C_{27}H_{23}N_2O_4P$ (470.46): C, 68.93; H, 4.93; N, 5.95. Found: C, 69.04; H, 4.93; N, 6.02%. **Major isomer** (*Z*)-**3a** (74%): $^1$H NMR (300.1 MHz): δ 2.90 (1H, dd, $^3J_{HH}$=10.5 Hz, $^3J_{PH}$=16.0 Hz, P=C-C*H*), 3.17 and 3.77 (6H, 2s, 2xOCH$_3$), 5.46 (1H, d, $^3J_{HH}$=10.5 Hz, C*H*(CN)$_2$), 7.52–7.77 (15H, m, 3xC$_6$H$_5$). $^{13}$C NMR (75.5 MHz): δ 24.80 (d, $^3J_{PC}$=4.9 Hz, *C*H(CN)$_2$), 39.66 (d, $^1J_{PC}$=128.8 Hz, P=*C*), 46.88 (d, $^2J_{PC}$=14.5 Hz, P=C-*C*H), 49.34 and 52.61 (2s, 2xOCH$_3$), 113.86 and 113.90 (2s, 2xCN), 125.64 (d, $^1J_{PC}$=92.8 Hz, C$_{ipso}$), 128.91 (d, $^3J_{PC}$=12.3 Hz, C$_{meta}$), 132.63 (d, $^4J_{PC}$=2.6 Hz, C$_{para}$), 139.91 (d, $^2J_{PC}$=9.8 Hz, C$_{ortho}$), 169.34 (d, $^2J_{PC}$=12.3 Hz, P-C=*C*), 171.11 (d, $^3J_{PC}$=4.0 Hz, C=O, ester). $^{31}$P NMR (121.5 MHz): δ 22.90 (Ph$_3$P$^+$-C). **Minor isomer** (*E*)-**3a** (26%): $^1$H NMR (300.1 MHz): δ 2.95 (1H, dd, $^3J_{HH}$=10.5 Hz, $^3J_{PH}$=15.6 Hz, P=C-C*H*), 3.58 and 3.76 (6H, 2s, 2xOCH$_3$), 4.91(1H, d, $^3J_{HH}$=10.5 Hz, C*H*(CN)$_2$), 7.52–7.77 (15H, *m*, 3xC$_6$H$_5$). $^{13}$C NMR (75.5 MHz): δ 26.37 (d, $^3J_{PC}$=5.3 Hz, *C*H(CN)$_2$), 40.75 (d, $^1J_{PC}$=137.3 Hz, P=*C*), 46.20 (d, $^2J_{PC}$=14.2 Hz, P=C-*C*H), 50.35 and 52.58 (2s, 2xOCH$_3$), 113.53 and 113.63 (2s, 2xCN), 125.13 (d, $^1J_{PC}$=92.9 Hz, C$_{ipso}$), 128.98 (d, $^3J_{PC}$=12.3 Hz, C$_{meta}$), 132.63 (d, $^4J_{PC}$=2.6 Hz, C$_{para}$), 133.96 (d, $^2J_{PC}$=9.8 Hz, C$_{ortho}$), 169.59 (d, $^2J_{PC}$=16.1 Hz, P-C=*C*), 171.48 (d, $^3J_{PC}$=4.8 Hz, C=O, ester). $^{31}$P NMR (121.5 MHz): δ 23.60 (Ph$_3$P$^+$-C).

**Diethyl 2-(dicyanomethyl)-3-(triphenylphosphanylidene)butanedioate** (**3b**)**.** The yield was 0.45 g, 91%, mp 169–172 °C, IR (KBr) ($\nu_{max}$, cm$^{-1}$): 2250 (CN), 1727 and 1620 (C=O). MS (*m/z*, %): 453 (M$^+$-OEt, 5), 434 (9), 433 (100), 425 (7), 262 (11), 183 (39), 108 (18), 77 (13). Anal. Calcd for $C_{29}H_{27}N_2O_4P$ (498.51): C, 69.87; H, 5.46; N, 5.62. Found: C, 69.80; H, 5.49; N, 5.58%. **Major isomer** (*Z*)-**3b** (75%): $^1$H NMR (300.1 MHz): δ 0.47 and 1.26 (6H, 2t, $^3J_{HH}$=7.1 Hz, 2xOCH$_2$C*H*$_3$), 2.88 (1H, dd, $^3J_{HH}$=10.5 Hz, $^3J_{PH}$=16.1 Hz, P=C-C*H*), 3.71 and 4.25 (4H, 2q, *J*=7.1 Hz, 2xOC*H*$_2$CH$_3$), 5.45 (1H, d, $^3J_{HH}$=10.5 Hz, C*H*(CN)$_2$), 7.48–7.80 (15H, m, 3xC$_6$H$_5$). $^{13}$C NMR (75.5 MHz): δ 13.80 and 14.06 (2s, 2xCH$_3$), 24.83 (d, $^3J_{PC}$=5.2 Hz, *C*H(CN)$_2$), 39.56 (d, $^1J_{PC}$=129.1 Hz, P=*C*), 46.92 (d, $^2J_{PC}$=15.1 Hz, P=C-*C*H), 58.02 and 61.84 (2s, 2xOC*H*$_2$CH$_3$), 114.06 and 114.03 (2s, 2xCN), 125.83 (d, $^1J_{PC}$=92.8 Hz, C$_{ipso}$), 128.82 (d, $^3J_{PC}$=12.1 Hz, C$_{meta}$), 132.57 (d, $^4J_{PC}$=2.2 Hz, C$_{para}$), 134.0 (d, $^2J_{PC}$=9.7 Hz, C$_{ortho}$), 168.95 (d, $^2J_{PC}$=12.1 Hz, P-C=*C*), 170.68 (d, $^3J_{PC}$=3.7 Hz, C=O, ester). $^{31}$P NMR (121.5 MHz): δ 22.80 (Ph$_3$P$^+$-C). **Minor isomer** (*E*)-**3b** (25%): $^1$H NMR (300.1 MHz): δ1.20 and 1.30 (6H, 2t, $^3J_{HH}$=7.1 Hz, 2xOCH$_2$C*H*$_3$), 2.94 (1H, dd, $^3J_{HH}$=10.3 Hz, $^3J_{PH}$=17.7 Hz, P=C-*CH*), 4.13 and 4.31 (4H, 2m, 2xABX$_3$ system, 2xOC*H*$_2$CH$_3$), 4.93 (1H, d, $^3J_{HH}$=10.3 Hz, C*H*(CN)$_2$), 7.48–7.80 (15H, m, 3xC$_6$H$_5$). $^{13}$C NMR (75.5 MHz): δ 14.14 and 14.91 (2s, 2xCH$_3$), 26.40 (d, $^3J_{PC}$=5.2 Hz, *C*H(CN)$_2$), 40.83 (d,

$^{1}J_{PC}$=137.4 Hz, P=*C*), 46.39 (d, $^{2}J_{PC}$=14.2 Hz, P=C-*C*H), 58.62 and 61.91 (2s, 2xO*C*H$_2$CH$_3$), 113.75 and 113.64 (2s, 2xCN), 125.31 (d, $^{1}J_{PC}$=92.8 Hz, $C_{ipso}$), 128.91 (d, $^{3}J_{PC}$=12.1 Hz, $C_{meta}$), 132.57 (d, $^{4}J_{PC}$=2.2 Hz, $C_{para}$), 134.0 (d, $^{2}J_{PC}$=9.7 Hz, $C_{ortho}$), 169.20 (d, $^{2}J_{PC}$=17.3 Hz, P-C=*C*), 171.04 (d, $^{3}J_{PC}$=3.7 Hz, C=O, ester). $^{31}$P NMR (202.4 MHz): δ 23.61(Ph$_3$P$^+$-C).

**Di- *tert*-butyl 2-(dicyanomethyl)-3-(triphenylphosphanylidene)butanedioate** (**3c**)**.** The yield was 0.53 g, 96%, mp 158–160 °C, IR (KBr) ($\nu_{max}$, cm$^{-1}$): 2247 (CN), 1723 and 1614 (C=O). MS (*m/z*, %): 554 (M$^+$, 7), 490 (15), 489 (35), 337 (100), 262 (22), 183 (38), 108 (17), 77 (8), 57 (75). Anal. Calcd for $C_{33}H_{35}N_2O_4P$ (554.62): C, 71.46; H, 6.36; N, 5.05. Found: C, 71.55; H, 6.37; N, 4.98%.

**Major isomer** (*Z*)**-3c.** (79%): $^{1}$H NMR (300.1 MHz), δ 0.95 and 1.50 (18H, 2s, 2x CMe$_3$), 2.74 (1H, dd, $^{3}J_{HH}$=10.4 Hz, $^{3}J_{PH}$=16.2 Hz, P=C-C*H*), 5.44 (1H, d, $^{3}J_{HH}$=10.4 Hz, C*H*(CN)$_2$), 7.52–7.81 (15H, m, 3x$C_6H_5$). $^{13}$C NMR (75.5 MHz), δ 24.91 (d, $^{3}J_{PC}$=4.6 Hz, *C*H(CN)$_2$), 28.00 and 28.22 (2s, 2x CMe$_3$), 39.54 (d, $^{1}J_{PC}$=129.8 Hz, P=C), 47.83 (d, $^{2}J_{PC}$=15.1 Hz, P=C-*C*H), 78.09 and 82.32 (2s, OCMe$_3$), 114.46 and 114.27 (2s, 2xCN), 126.40 (d, $^{1}J_{PC}$=92.4 Hz, $C_{ipso}$), 128.61 (d, $^{3}J_{PC}$=12.1 Hz, $C_{meta}$), 132.34 (d, $^{4}J_{PC}$=2.3 Hz, $C_{para}$), 134.12 (d, $^{2}J_{PC}$=9.7 Hz, $C_{ortho}$), 168.48 (d, $^{2}J_{PC}$=11.7 Hz, P-C=*C*), 169.78 (d, $^{3}J_{PC}$=4.5 Hz, C=O). $^{31}$P NMR (121.5 MHz): δ 22.40 (Ph$_3$P$^+$-C).

**Minor isomer** (*E*)**-3c.** (21%): $^{1}$H NMR (300.1 MHz), δ 1.45 and 1.47 (18H, 2s, 2x CMe$_3$), 2.71 (1H, dd, $^{3}J_{HH}$=10.4 Hz, $^{3}J_{PH}$=16.3 Hz, P=C-C*H*), 5.00 (1H, d, $^{3}J_{HH}$=10.4 Hz, C*H*(CN)$_2$), 7.52–7.81 (15H, m, 3x$C_6H_5$). $^{13}$C NMR (75.5 MHz), δ 27.76 and 29.60 (2s, 2 C*Me$_3$*), 25.00 (d, $^{3}J_{PC}$=5.3 Hz, *C*H(CN)$_2$), 41.31 (d, $^{1}J_{PC}$=137.5 Hz, P=C), 46.93 (d, $^{2}J_{PC}$=14.7 Hz, P=C-*C*H), 78.49 and 82.30 (2s, OCMe$_3$), 113.82 and 113.98 (2s, 2 CN), 125.80 (d, $^{1}J_{PC}$=92.7 Hz, $C_{ipso}$), 128.77 (d, $^{3}J_{PC}$=11.2 Hz, $C_{meta}$), 132.34 (d, $^{4}J_{PC}$=2.3 Hz, $C_{para}$), 133.99 (d, $^{2}J_{PC}$=9.6 Hz, $C_{ortho}$), 168.50 (d, $^{2}J_{PC}$=11.1 Hz, P-C=*C*), 169.56 (d, $^{3}J_{PC}$=4.9 Hz, C=O). $^{31}$P NMR (121.5 MHz): δ 23.87 (Ph$_3$P$^+$-C).

**Dimethyl 2-(ethyl-1-cyanoethanoat-1-yl)-3-(triphenylphosphanylidene)butanedioate** (**3d**)**.** The yield was 0.48 g, 93%, mp 143–145 °C, IR (KBr) ($\nu_{max}$, cm$^{-1}$): 2235 (CN), 1736 and 1621 (C=O). MS (*m/z*, %): 517 (M$^+$, 4), 416 (20), 404 (22), 262 (100), 187 (72), 108 (15). Anal. Calcd for $C_{29}H_{28}NO_6P$ (517.51): C, 67.31; H, 5.45; N, 2.71. Found: C, 67.39; H, 5.48; N, 2.65%.

**Major isomer** (*Z*)**-3d.** (64%): $^{1}$H NMR (300.1 MHz): δ 1.21 (3H, t, $^{3}J_{HH}$=7.1 Hz, OCH$_2$C*H$_3$*), 3.05 (1H, dd, $^{3}J_{HH}$=10.9 Hz, $^{3}J_{PH}$=16.6 Hz, P=C-C*H*), 3.14 and 3.65 (6H, 2s, 2xOCH$_3$), 4.13 (2H, m, ABX$_3$ system, O*CH$_2$*CH$_3$), 5.02 (1H, d, $^{3}J_{HH}$=10.9 Hz, C*H*(CNCO$_2$Et)), 7.50–7.79 (15H$_{arom}$, m, 3x$C_6H_5$). $^{13}$C NMR (75.5 MHz): δ 13.85 (s, OCH$_2$*C*H$_3$), 39.27 (d, $^{3}J_{PC}$=3.9 Hz, *C*H(CNCO$_2$Et)), 39.39 (d, $^{1}J_{PC}$=128.3 Hz, P=*C*), 44.37 (d, $^{2}J_{PC}$=14.41 Hz, P=C-*CH*), 49.10 and 52.15 (2s, 2xOCH$_3$), 62.23 (s, OCH$_2$), 117.32 (s, CN), 126.39 (d, $^{1}J_{PC}$=92.4 Hz, $C_{ipso}$), 128.68 (d, $^{3}J_{PC}$=12.3 Hz, $C_{meta}$), 132.25 (d, $^{4}J_{PC}$=2.8 Hz, $C_{para}$), 134.03 (d, $^{2}J_{PC}$=9.7 Hz, $C_{ortho}$), 166.26 (s, C=O, CO$_2$Et), 169.54 (d, $^{2}J_{PC}$=12.8 Hz, P-C=*C*), 173.24 (d, $^{3}J_{PC}$=4.6 Hz, C=O). $^{31}$P NMR (202.4 MHz): δ 23.20 (Ph$_3$P$^+$-C).

**Minor isomer** (*E*)**-3d.** (36%): $^{1}$H NMR (300.1 MHz): δ 1.23 (3H, t, $^{3}J_{HH}$=7.1 Hz, OCH$_2$C*H$_3$*), 3.10 (1H, dd, $^{3}J_{HH}$=11.2 Hz, $^{3}J_{PH}$=16.5 Hz, P=C-C*H*), 3.56 and 3.64 (6H, 2s, 2xOCH$_3$), 4.13 (2H,

m, $ABX_3$ system, $OCH_2CH_3$), 4.63 (1H, d, $^3J_{HH}$=11.2 Hz, C*H*($CNCO_2Et$)), 7.50–7.79 (15H, m, $3xC_6H_5$). $^{13}C$ NMR (75.5 MHz): δ 13.85 (s, $OCH_2CH_3$), 40.75 (d, $^3J_{PC}$=3.9 Hz, *C*H($CNCO_2Et$)), 40.31 (d, $^1J_{PC}$=136.9 Hz, P=*C*), 43.62 (d, $^2J_{PC}$=14.5 Hz, P=C-*C*H), 50.23 and 52.15 (2s, $2xOCH_3$), 62.37 (s, $OCH_2CH_3$), 117.04 (s, CN), 125.80 (d, $^1J_{PC}$=92.5 Hz, $C_{ipso}$), 128.76 (d, $^3J_{PC}$=12.4 Hz, $C_{meta}$), 132.25 (d, $^4J_{PC}$=2.8 Hz, $C_{para}$), 134.05 (d, $^2J_{PC}$=9.7 Hz, $C_{ortho}$), 166.02 (s, C=O, $CO_2Et$), 170.23 (d, $^2J_{PC}$=17.8 Hz, P-C=*C*), 173.69 (d, $^3J_{PC}$=5.1 Hz, C=O). $^{31}P$ NMR (121.5 MHz): δ 23.57 ($Ph_3P^+$-C).

**Diethyl 2-(ethyl-1-cyanoethanoat-1-yl)-3-(triphenylphosphanylidene)butanedioate** (**3e**)**.** The yield was 0.49 g, 90%, mp 120–123 °C, IR (KBr) ($\nu_{max}$, $cm^{-1}$): 2230 (CN), 1742, 1725 and 1619 (C=O). MS (*m/z*, %): 546 ($M^+$+1, 2), 534 (15), 522 (23), 262 (65), 187 (79), 108 (100). Anal. Calcd for $C_{31}H_{32}NO_6P$ (545.56): C, 68.25; H, 5.91; N, 2.57. Found: C, 68.57; H, 5.79; N, 2.65%.

**Major isomer** (*Z*)**-3e.** (67%): $^1H$ NMR (300.1 MHz): δ 0.46 (3H, t, $^3J_{HH}$=7.0 Hz, $OCH_2CH_3$), 1.17–1.24 (6H, m, $2xCH_3$), 3.05 (1H, dd, $^3J_{HH}$=10.1 Hz, $^3J_{PH}$=16.5 Hz, P=C-C*H*), 3.05–3.11 and 4.00–4.20 (6H, 2m, $3xABX_3$ system, $3xOCH_2CH_3$), 5.01 (1H, d, $^3J_{HH}$=10.1 Hz, C*H*($CNCO_2Et$)), 7.50–7.80 (15H, m, $3xC_6H_5$). $^{13}C$ NMR (75.5 MHz): δ 13.81, 14.08 and 15.02 (3s, $3xOCH_2CH_3$), 39.27 (d, $^1J_{PC}$=128.5 Hz, P=*C*), 39.35 (d, $^3J_{PC}$=3.9 *C*H($CNCO_2Et$)), 44.47 (d, $^2J_{PC}$=14.5 Hz, P=C-*C*H), 57.67, 61.12 and 62.14 (3s, $3xOCH_2CH_3$), 117.49 (s, CN), 126.66 (d, $^1J_{PC}$=92.4 Hz, $C_{ipso}$), 128.56 (d, $^3J_{PC}$=12.3 Hz, $C_{meta}$), 132.14 (d, $^4J_{PC}$=2.6 Hz, $C_{para}$), 134.13 (d, $^2J_{PC}$=9.8 Hz, $C_{ortho}$), 166.39 (s, C=O, $CO_2Et$), 169.15 (d, $^2J_{PC}$=12.8 Hz, P-C=*C*), 172.83 (d, $^3J_{PC}$=4.7 Hz, C=O). $^{31}P$ NMR (121.5 MHz): δ 23.19 ($Ph_3P^+$-C). **Minor isomer** (*E*)**-3e** (33%): $^1H$ NMR (300.1 MHz): δ 0.46 (3H, t, $^3J_{HH}$=7.0 Hz, $OCH_2CH_3$), 1.17–1.24 (6H, m, $2xCH_3$), 3.11 (1H, dd, $^3J_{HH}$=11.0 Hz, $^3J_{PH}$=16.6 Hz, P=C-C*H*), 3.71–3.78 and 4.00–4.20 (6H, 2m, $3xABX_3$ system, $3xOCH_2CH_3$), 4.64 (1H, d, $^3J_{HH}$=11.0 Hz, C*H*($CNCO_2Et$)), 7.50–7.80 (15H, m, $3xC_6H_5$). $^{13}C$ NMR (75.5 MHz): δ 13.87, 14.15 and 14.95 (3s, $3xOCH_2CH_3$), 40.44 (d, $^1J_{PC}$=136.9 Hz, P=*C*), 40.80 (d, $^3J_{PC}$=3.9 *C*H($CNCO_2Et$)), 43.84 (d, $^2J_{PC}$=14.3 Hz, P=C-*C*H), 58.30, 61.19 and 62.29 (3s, $3xOCH_2CH_3$), 117.14 (s, CN), 126.03 (d, $^1J_{PC}$=92.4 Hz, $C_{ipso}$), 128.67 (d, $^3J_{PC}$=12.2 Hz, $C_{meta}$), 132.14 (d, $^4J_{PC}$=2.6 Hz, $C_{para}$), 134.13 (d, $^2J_{PC}$=9.8 Hz, $C_{ortho}$), 166.13 (s, C=O, *C*$O_2Et$), 169.86 (d, $^2J_{PC}$=17.7 Hz, P-C=*C*), 173.24 (d, $^3J_{PC}$=5.1 Hz, C=O). $^{31}P$ NMR (121.5 MHz): δ 23.73 ($Ph_3P^+$-C).

**Di-*tert*- butyl 2-(ethyl 1-cyanoethanoat-1-yl)-3-(triphenylphosphanylidene)butanedioate** (**3f**)**.** The yield was 0.57 g, 95%, mp 144–146 °C, IR (KBr) ($\nu_{max}$, $cm^{-1}$): 2270 (CN), 1727, 1730 and 1616 (C=O). MS (*m/z*, %): 601 ($M^+$, 10), 500 (22), 489 (20), 262 (23), 183 (59), 108 (18), 77 (9), 57 (100). Anal. Calcd for $C_{35}H_{40}NO_6P$ (601.67): C, 69.87; H, 6.70; N, 2.33. Found: C, 69.75; H, 6.708; N, 2.41%. **Major isomer** (*Z*)**- 3f** (70%): $^1H$ NMR (300.1 MHz), δ 0.95 and 1.43 (18H, 2s, 2x $CMe_3$), 1.19 (3H, t, $^3J_{HH}$=7.1 Hz, $OCH_2CH_3$), 2.84 (1H, dd, $^3J_{HH}$=10.9 Hz, $^3J_{PH}$=18.7 Hz, P=C-C*H*), 4.10 (2H, m, $ABX_3$ system, $OCH_2CH_3$), 5.01 (1H, d, $^3J_{HH}$=10.9 Hz, C*H*($CNCO_2Et$)), 7.46–7.85 (15H, m, $3xC_6H_5$). $^{13}C$ NMR (75.5 MHz), δ 13.75 (s, $OCH_2CH_3$), 28.05 and 28.29 (2s, 2x $CMe_3$), 39.07 (d, $^1J_{PC}$=129.1 Hz, P=C), 39.41 (d, $^3J_{PC}$=3.9 Hz, *C*H($CNCO_2Et$)), 45.37 (d, $^2J_{PC}$=14.8 Hz, P=C-*C*H), 61.85 (s, $OCH_2CH_3$), 77.38 and 80.92 (2s, 2x O*C*$Me_3$), 117.95 (s, CN), 126.49 (d, $^1J_{PC}$=92.4 Hz, $C_{ipso}$), 128.36 (d, $^3J_{PC}$=11.9 Hz, $C_{meta}$), 131.96 (d, $^4J_{PC}$=2.4 Hz, $C_{para}$), 134.24 (d, $^2J_{PC}$=9.5 Hz, $C_{ortho}$), 166.40 (C=O, *C*$O_2Et$), 168.57 (d, $^2J_{PC}$=12.3 Hz, P-C=*C*), 171.96

(d, $^3J_{PC}$=5.0 Hz, C=O). $^{31}$P NMR (121.5 MHz): δ 22.56 ($Ph_3P^+$-C). **Minor isomer** (*E*)- **3f** (30%): $^1$H NMR (300.1 MHz), δ 1.41 and 1.45 (18H, 2s, 2xCMe$_3$), 1.21 (3H, t, $^3J_{HH}$=7.1 Hz, OCH$_2$C*H$_3$*), 2.91 (1H, dd, $^3J_{HH}$=10.8 Hz, $^3J_{PH}$=17.1 Hz, P=C-*CH*), 4.10 (2H, m, ABX$_3$ system, O*CH$_2$*CH$_3$), 4.71 (1H, d, $^3J_{HH}$=10.8 Hz, C*H*(CNCO$_2$Et)), 7.51–7.81 (15xH$_{arom}$, m, 3x C$_6$H$_5$). $^{13}$C NMR (75.5 MHz), δ 13.75 (s, OCH$_2$CH$_3$), 28.17 and 28.84 (2s, 2x C*Me$_3$*), 40.48 (d, $^3J_{PC}$=3.9 Hz, *C*H(CNCO$_2$Et)), 41.01 (d, $^1J_{PC}$=136.3 Hz, P=C), 44.28 (d, $^2J_{PC}$=14.7 Hz, P=C-*C*H), 62.08 (s, OCH$_2$), 77.63 and 80.86 (2s, 2x OC*Me$_3$*), 117.37 (s, CN), 127.16 (d, $^1J_{PC}$=92.5 Hz, C$_{ipso}$), 128.52 (d, $^3J_{PC}$=11.5 Hz, C$_{meta}$), 131.96 (d, $^4J_{PC}$=2.4 Hz, C$_{para}$), 134.11 (d, $^2J_{PC}$=9.4 Hz, C$_{ortho}$), 166.08 (C=O), 170.07 (d, $^2J_{PC}$=17.9 Hz, P-C=*C*), 171.79 (d, $^3J_{PC}$=5.2 Hz, C=O). $^{31}$P NMR (121.5 MHz): δ 22.40 ($Ph_3P^+$-C).

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