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Synthesis of heterocyclic stable phosphorus ylides from reaction between triphenylphosphine and activated acetylenic esters in the presence of biological active NH heterocyclic compounds

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ABSTRACT

Triphenylphosphine reacts with dialkyl acetylenedicarboxylates in the presence of biological active NH heterocyclic compounds, such as (2H) -3-pyridazinone, 1-phenyl-3-pyrazolid- inone, 2,4-thiazolinedione, Rhodanine, 4,5,6,7-tetrahydroindazole and 3-methyl- pyrazole to generate stable phosphorus ylides. These compounds exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon-carbon partical double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group.

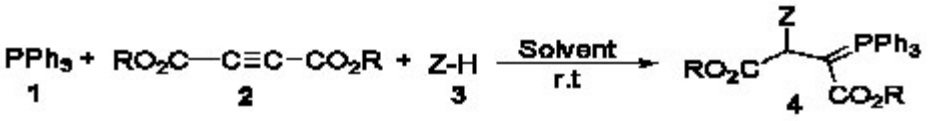
Key words: Activated acetylenic esters; NH heterocyclic compounds; Triphenyl- phosphine; Stable phosphorus ylides; Geometrical isomers; biological activity.

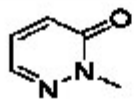
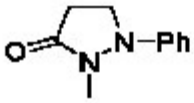
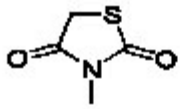
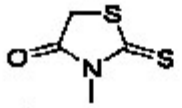
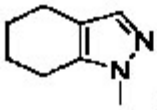
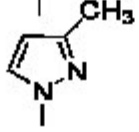
INTRODUCTION

Phosphorus-carbon bond formation[1-15] is an active and important research area, as new reactions are continuously being developed for the preparation of organophosphorus compounds such as phosphinates and phosphonates[16-24]. Over the last few years, the quest for the synthetic efficiency has gained remarkable importance, partly due to the need reduce waste[25]. Given the increasing industrial, biological and synthetic impact of organophosphorus compounds[26-30]. The successful attack by nucleophilic trivalent phosphorus on a carbon atom is facilitated when the latter is part of, or conjugated with, a carbonyl group, or when it is part of an unsaturated bond otherwise activated[27-29]. There are many studies on the reaction between trivalent phosphorus nucleophiles and α, β–unsaturated carbonyl compounds in the presence of a proton source such as alcohol or phenol.[31,32] Here we wish to report a simple one-pot synthesis of heterocyclic compounds-containing stable phosphorus ylides. Previously, the pyrazole and thiazole moieties and their derivatives have been used commercially as pharmaceuticals, pesticides and dyestuffs[33]. Thus, the reaction of triphenylphosphine 1 with dialkyl acetylenedicarboxylates 2 in the presence of NH heterocyclic compounds 3 such as 3-methylpyrazole and etc were undertaken to generate the corresponding stable heterocyclic phosphorus ylides 4 in excellent yields (Scheme 1).

RESULTS AND DISCUSSION

In the current work, stable phosphorus ylides from reaction between triphenylphosphine 1 and dialkyl acetylenedicarboxylates 2 in the presence of N-H acids 3, such as (2H)-3-pyridazinone, 1-phenyl-3-pyrazolidinone, 2,4-thiazolinedi- one, Rhodanine, 4,5,6,7-tetrahydroindazole and 3-methylpyrazole led to 4 in excellent yields (see Scheme 1). The reactions (4a-m) were carried out in ethyl acetate solvent at room temperature and were finished within a few minutes. The ^{1}H and ^{13}C NMR spectrum of the crude product clearly indicated the formation of compounds 4a-m. Any products other than 4a-m could not be detected by NMR spectroscopy. The structures of compounds 4a-m were deduced from their IR, ^{1}H, ^{13}C, ^{31}P NMR spectra, Mass spectrometry and elemental analysis. The mass spectra of compounds 4a-m displayed molecular ion peaks at appropriate values, which were consistent with 1:1:1 adducts of NH heterocyclic compounds, dialkyl acetylenedicarboxylates and triphenylphosphine. Although the presence of the ^{31}P nucleus complicates both the ^{1}H and ^{13}C NMR spectra of 4a, it helps in assignment of the signals by long-range couplings with the ^{1}H and ^{13}C nuclei (see Experimental section). The ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides 4a-m are consistent with the presence of two isomers. The ylides moieties of these compounds are strongly conjugated with the adjacent carbonyl group and rotation around the partial double bond in (*E*)-4 and (*Z*)-4 geometrical isomers is slow on the NMR timescale at ambient temperature (see Scheme 2). As can be seen, only one geometrical isomer was observed for di-tert-butyl derivatives of 4, presumeably, because of the bulky tert-butyl groups. (Scheme 2).

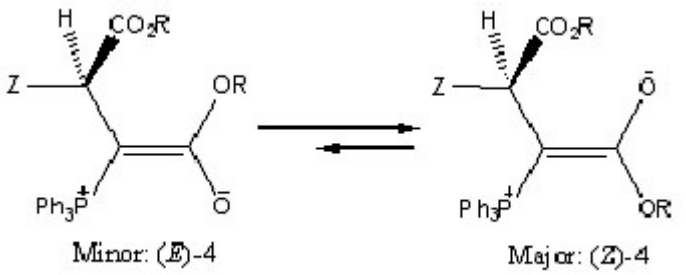


4	Z	R	%Yield
a		Me	90
b		Me	93
c		Et	91
d		Bu^{t}	96
e		Me	94
f		Et	91
g		Bu^{t}	96
h		Me	90
i		Bu^{t}	93
j		Me	87
k		Me	94
l		Et	92
m		Bu^{t}	96

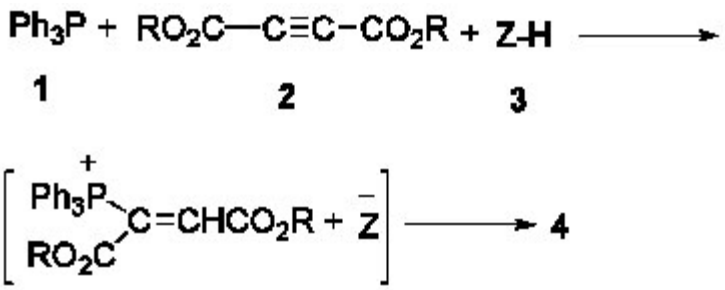
Scheme 1

On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[3-7] it is reasonable to assume that phosphorus ylide 4 results from the initial addition of triphenylphosphine to the acetylenic esters and subsequent protonation of the 1:1 adduct by the NH heterocyclic compounds to form phosphoranes 4 (Scheme 3).

The ^{1}H NMR 500 MHz spectra of 4a showed four sharp lines at δ = 3.14, 3.72, 3.61 and



Scheme 2



Scheme 3

3.66 ppm arising from methoxy protons. Methine protons appeared as two doublet peaks at δ= 5.64 ppm (1H, d, $^3J_{PH}$=17.0 Hz, P-C-C*H*) and 5.75 ppm (1H, d, $^3J_{PH}$=18.9 Hz, P-C-C*H*) respectively for the E and Z geometrical isomers. The aromatic protons appeared as a multiplet at δ = 6.65–7.90 ppm (18H, m, $3C_6H_5$ and $C_4H_4N_2O$). The ^{13}C NMR spectrum of 4a displayed 28 distinct resonances in a good agreement with the mixture of two conformational isomers. The ^{1}H and ^{13}C NMR spectra of compounds 4b-m are similar to those of 4a, except for signals from the ester group which appear as characteristic resonance lines with the corresponding chemical shifts. The structural assignments of 4a-m were made on the basis of the ^{1}H and ^{13}C NMR spectra that were supported by their IR spectra. The carbonyl region of the spectra exhibited two distinct absorption bands for each compound related to ester groups of yilde moiety (see Experimental section).

Briefly, we have prepared novel phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong NH heterocyclic compounds. The present method carries the advantage that, not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modifications. Heterocyclic compounds-containing stable phosphorus ylides **4a-m** may be considered as potentially useful synthetic intermediates. It seems that, the procedure described here may be employed as an acceptable method for the

preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer respectively. Also, the ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained from a BRUKER DRX-500 AVANCE instrument with $CDCl_3$ as an solvent at 500.1, 125.8, and 202.4 MHz respectively. Elemental analyses for C, H, N were performed using a Heraeus CHN-O-Rapid analyzer. In addition, the mass spectra were recorded on a GCMS-QP 5050A mass spectrometer operating at an ionization potential of 70 eV. (2H)-3-pyridazinone, 1-phenyl-3-pyrazolidinone, 2,4-thiazolinedione, Rhodanine, 4,5,6,7-tetrahydroindazole, 3-methylpyrazole dialkyl acetylenedicarboxylates and triphenlphosphine, were purchsed from Fluka, (Buchs, Switzerland) and used without further purifications.

General Procedures (Exemplified by 4a)

Preparation of dimethyl 2-(3-pyridazinone-2-yl)-3-(triphenylphosphanylidene) butanedioate (4a)

To a magnetically stirred solution of triphenylphosphine (0.26 g or 1 mmol) and (2H)-3-pyridazinone (0.96 g or 1 mmol) in 10 mL of dry ethyl acetate was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.14g or 1 mmol) in 5 mL of dry ethyl acetate over 10 min. After a few minutes stirring at room temperature, the product was filtered and washed with cold diethyl ether (3 × 5 mL).

White powder, m.p 93-95°C, 0.46 g, yield 90%, IR (ν_{max}, cm^{-1}): 1733 and 1664 (C=O). 500 (M^{+},7), 438 (M-2OMe, 37), 382 (M-2CO_2Me 46), 262 (PPh_3, 80), 183 (PPh_2, 48), 108 (PPh, 43), 77 (Ph, 35). Anal. calcd. for $C_{28}H_{25}N_2O_5P$ (500): C, 67.17; H, 5.04; N, 5.60 %. Found: C, 67.21; H, 4.95; N, 5.67 %.

Major isomer *Z*-4a (60%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.14 and 3.72 (6H, 2s, 2OCH_3), 5.64 (1H, d, $^{3}J_{PH}$ = 17.0 Hz, P=C-C*H*), 6.65-7.90 (18Haro, m, 3C_6H_5 and $C_4H_3N_2O$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 42.75 (d, $^{1}J_{PC}$ = *126.8* Hz, P=*C*), 49.34 and 52.30 (2s, 2OCH_3), 63.72 (d, $^{2}J_{PC}$=*16.0* Hz, P-C-*C*H), 108.89 (1C, $C_4H_3N_2O$), 126.37 (d, $^{1}J_{PC}$ = 92.0 Hz, C_{ipso}), 127.84 (d, $^{3}J_{PC}$ = 11.9 Hz, C_{meta}), 132.19 (d, $^{4}J_{PC}$ = 2.1 Hz, C_{para}), 133.57 (1C, $C_4H_3N_2O$), 133.28 (d, $^{2}J_{PC}$ = 9.0 Hz, C_{ortho}), 147.55 and 162.13 (2C, $C_4H_3N_2O$), 165.42 (d, $^{3}J_{PC}$ = 15.7Hz, C=O), 171.57 (d, $^{2}J_{PC}$ = 13.5 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.12 (Ph_3P^{+}-C).

Minor isomer *E*-4a (40%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.61 and 3.66 (6H, 2s, 2OCH_3), 5.75 (1H, d, $^{3}J_{PH}$ = 18.9 Hz, P=C-C*H*), 6.65-7.90 (18Haro, m, 3C_6H_5 and $C_4H_3N_2O$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 42.86 (d, $^{1}J_{PC}$ = 136.0 Hz, P=C), 50.32 and 52.32 (2s, 2OCH_3), 63.57 (d, $^{2}J_{PC}$ = 15.8 Hz, P-C-*C*H), 108.93 (1C, $C_4H_3N_2O$), 125.67 (d, $^{1}J_{PC}$ = 92.1 Hz, C_{ipso}), 128.27 (d, $^{3}J_{PC}$ = 12.0 Hz, C_{meta}), 132.23 (d, $^{4}J_{PC}$ = 2.2 Hz, C_{para}), 134.13 (1C, $C_4H_3N_2O$), 133.59 (d, $^{2}J_{PC}$ = 9.8 Hz, C_{ortho}), 147.63 and 163.14 (2C, $C_4H_3N_2O$), 165.72 (d, $^{3}J_{PC}$ =14.8 Hz, C=O), 169.83 (d, $^{2}J_{PC}$ = 12.5 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.97 (Ph_3P^{+}-C).

dimethyl-2-(1-phenyl-3-pyrazolidinone-2-yl)-3-(triphenylphosphanylidene) butanedioate (4b).

White powder, m.p 166-168°C, 0.53g, yield 93%, IR (ν_{max}, cm^{-1}) 1753 and 1676 (C=O). MS (*m/z*, %): 446 (M-2CO_2Me, 17), 304 (M-PPh and Ph, 38), 262 (PPh_3, 76), 183 (PPh_2, 36), 108 (PPh, 43), 77 (Ph, 14). Anal. calcd. for $C_{33}H_{31}N_2O_5P$ (566): C, 70.12; H,5.56; N, 5.02%. Found: C, 69.96; H, 5.48; N, 4.95%.

Major isomer *Z*-4b (68%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.43(2H, m, H_2C-CO), 3.20(3H, s, OCH_3), 3.55(2H, m, H_2C-N), 3.81 (3H, s, OCH_3), 4.97 (1H_{bro}, P-C-C*H*), 6.99–7.71 (20H_{arom}, m, 4C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 29.65 and 30.03 (2C, $C_9H_9N_2O$), 38.18 (d, $^{1}J_{PC}$ = 128.8 Hz, P=C), 49.68 and 52.08 (2s, 2O*C*H_3), 59.79 (d, $^{2}J_{PC}$ = 16.2 Hz, P-C-*C*H), 116.56, 119.76, 123.03, 126.17 and 126.91 (5C, $C_9H_9N_2O$), 126.54 (d, $^{1}J_{PC}$ = 92.9 Hz, C_{ipso}), 128.50 (d, $^{3}J_{PC}$ = 12.3 Hz, C_{meta}), 131.85 (C_{para}), 132.07 (1C, $C_9H_9N_2O$), 133.73 (d, $^{2}J_{PC}$ = 9.8 Hz, C_{ortho}), 170.43 (d, $^{3}J_{PC}$ = 16.8 Hz, C=O), 171.89 (d, $^{2}J_{PC}$ = 17.6 Hz, P-C=*C*), 176.59 (1C, $C_9H_9N_2O$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.56 (Ph_3P^{+}-C).

Minor isomer *E*-4b (32%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.52(2H,

m, H_2C-CO), 3.44(2H, m, H_2C-N), 3.74 and 3.79 (6H, 2s, 2OCH_3), 4.93 (1H_{bro}, P-C-C*H*), 6.99–7.71 (20H_{arom}, m, 4C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 29.54 and 29.96 (2C, $C_9H_9N_2O$), 39.76 (d, $^1J_{PC}$ = 139.4 Hz, P=C), 52.01 and 52.27 (2s, 2O*C*H_3), 60.20 (d, $^2J_{PC}$ = 15.2 Hz, P-C-*C*H), 116.52, 119.80, 123.07, 126.23 and 126.86 (5C, $C_9H_9N_2O$), 126.17 (d, $^1J_{PC}$ = 92.0 Hz, C_{ipso}), 128.60 (d, $^3J_{PC}$ = 11.8 Hz, C_{meta}), 131.69 (C_{para}), 132.15 (1C, $C_9H_9N_2O$), 133.64 (d, $^2J_{PC}$ = 10.0 Hz, C_{ortho}), 172.02 (d, $^3J_{PC}$ = 14.3 Hz, C=O), 171.74 (d, $^2J_{PC}$ = 15.4 Hz, P-C=*C*), 177.11 (1C, $C_9H_9N_2O$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.90 (Ph_3P^+-C).

Diethyl-2-(1-phenyl-3-pyrazolidinone-2-yl)-3-(triphenylphosphanylidene) butanedioate (**4c**).

White powder, m.p 161-163°C, 0.54g, yield 91%, IR (õ$_{max}$, cm^{-1}) 1748 and 1662 (C=O). MS (*m/z*, %): 502 (M-2OEt , 50), 434 (M-PPh and OEt, 28), 330 (M-PPh_3, 7), 262 (PPh_3, 85), 183 (PPh_2, 83), 108 (PPh, 31). Anal. calcd. for $C_{35}H_{35}N_2O_5P$ (594): C, 71.35; H, 6.05; N, 4.64%. Found: C, 70.71; H, 5.95; N, 4.71%.

Major isomer *Z*-4c (66%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.36 and 1.27 (6H, 2t, $^3J_{HH}$ = 7.0 Hz, 2OCH_2CH_3), 2.41(2H, m, H_2C-CO), 3.48 and 3.54 (4H, 2m, 2ABX$_3$ system, 2OCH_2CH_3), 3.59(2H, m, H_2C-N), 4.26 (1H_{bro}, P-C-C*H*), 7.12-7.73 (20H_{arom}, m, 4C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.96 and 14.13 (2s, 2OCH_2CH_3), 29.61 and 30.09 (2C, $C_9H_9N_2O$), 37.89 (d, $^1J_{PC}$ = 128.9 Hz, P=C), 57.45 and 58.05 (2S, 2O*C*H_2CH_3), 59.98 (d, $^2J_{PC}$ = 14.8 Hz, P-C-*C*H), 116.59, 119.80, 122.96, 126.35 and 127.08 (5C, $C_9H_9N_2O$), 126.27 (d, $^1J_{PC}$ = 92.0 Hz, C_{ipso}), 128.35 (d, $^3J_{pc}$ = 12.1 Hz, C_{meta}), 131.63 (C_{para}), 132.07 (1C, $C_9H_9N_2O$), 133.88 (C_{ortho}), 170.69 (d, $^3J_{PC}$ = 17.7 Hz, C=O), 171.19 (d,.$^2J_{PC}$ = 16.3 Hz, P-C=*C*), 176.99 (1C, $C_9H_9N_2O$).^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.35 (Ph_3P^+-C)

Minor isomer *E*-4c (34%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.09 and 1.32 (6H, 2t, $^3J_{HH}$ = 7.2 Hz , 2OCH_2CH_3), 2.53(2H, m, H_2C-CO), 3.41(2H, m, H_2C-N), 3.91 and 4.06 (4H, 2m, 2ABX$_3$ system, 2OCH_2CH_3), 4.31 (1H_{bro}, P-C-C*H*), 7.12-7.73 (20H_{arom}, m, 4C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.13 and 14.73 (2s, 2OCH_2CH_3), 29,53 and 30.01 (2C, $C_9H_9N_2O$), 39.69 (d, $^1J_{PC}$ =133.3 Hz, P=C), 58.01 and 58.39 (2s, 2O*C*H_2CH_3), 60.41 (d, $^2J_{PC}$ = 15.1 Hz, P-C-*C*H), 116.51, 120.05, 123.20, 126.42 and 127.15 (5C, $C_9H_9N_2O$), 126.72 (d, $^1J_{PC}$=91.8 Hz, C_{ipso}), 128.54 (d, $^3J_{pc}$ = 12.0 Hz, C_{meta}), 129.19 (1C, $C_9H_9N_2O$), 131.76 (C_{para}), 132.14 (1C, $C_9H_9N_2O$), 133.88 (C_{ortho}), 169.98 (d, $^3J_{PC}$ =16.4 Hz, C=O), 170.12 (d, $^2J_{PC}$ = 15.9 Hz, P-C=*C*),177.26 (1C, $C_9H_9N_2O$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.52 (Ph_3P^+-C).

Di-tert-buthyl-2-(1-phenyl-3-pyrazolidinone-2-yl)-3-(triphenylphosphanylidene) butanedioate (4d)

White crystals, m.p. 176-178 °C, 0.62g, yield 96%; IR (ímax, cm-1): 1746 and 1671 (C=O). MS (*m/z*, %): 650 (M, 3), 386 (M-PPh_3, 38), 262 (PPh_3, 79), 183 (PPh_2, 43), 108 (PPh, 51). Anal. calcd. for $C_{39}H_{43}N_2O_5P$ (650): C, 71.08; H, 6.72; N, 4.28%. Found: C, 71.56; H, 6.68; N, 4.31%.

Major rotamer *Z*-4d

^{1}H NMR (500.1 MHz, $CDCl_3$), δ_H 0.80 and 1.49 (18H, 2s, 2OC*Me*3), 2.50(2H, m, H_2C-CO), 3.46(2H, m, H_2C-N), 4.67 (1H, d, $^3J_{PH}$ = 17.4 Hz, P-C-C*H*), 7.03-7.69 (20H_{arom}, m, 4C_6H_5). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ 28.16 and 28.43 (2OCMe_3), 29.76 and 30.12 (2C, $C_9H_9N_2O$), 37.63 (d, $^1J_{PC}$ = 127.2 Hz, P=C), 60.79 (d, $^2J_{PC}$ =14.9 Hz, P-C-*C*H), 80.60 and 80.83 (2s, 2O*C*Me_3), 116.61, 119.36, 121.17, 122.75 and 123.66 (5C, $C_9H_9N_2O$), 127.18 (d, $^1J_{PC}$ = 91.2 Hz, C_{ipso}), 128.31 (d, $^3J_{PC}$ = 11.8 Hz, C_{meta}), 131.56 (C_{para}), 132.22 (1C, $C_9H_9N_2O$), 133.82 (d, $^2J_{PC}$ = 9.4 Hz, C_{ortho}), 169.98(d, $^3J_{PC}$ = 11.6 Hz, C=O), 171.03 (d, $^2J_{PC}$ = 11.7 Hz, P-C=C), 177.74 (1C, $C_9H_9N_2O$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.29 (Ph_3P^+-C).

Dimethyl -2-(2,4-thiazolidinedione-2-yl)-3-(triphenylphosphanylidene) butaned- ioate (**4e**).

White crystals, m.p. 95-97 ºC, 0.48g, yield 94%; IR (ímax, cm-1): 1739 and 1685, 1662 and 1610 (C=O); MS, (m/z, %): 509 (M$^+$, 1), 334 (M-$C_3H_2O_2NS$ and CO_2Me, 29), 278 (M-3Ph, 69), 262 (PPh_3, 83), 183 (PPh_2, 86), 108 (PPh, 36). Anal. calcd. for $C_{27}H_{24}NO_6PS$ (521): C, 62.17; H, 4.64; N, 2.69 %. Found: C, 62.28; H, 4.60; N, 2.65%.

Major rotamer *Z*-4e (63%)

^{1}H NMR (500.1 MHz, $CDCl_3$), δ_H 3.11 and 3.70 (6H, 2s, 2OCH_3), 3.75 (2H, dd, $^2J_{HH}$ = 16.0, S-

CH_2), 4.78 (1H, d, $^3J_{PH}$ = 15.0 Hz, P-C-C*H*), 7.45-7.70 (15H_{arom}, m, 3C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 32.98 (1C, S-*C*H_2), 36.33 (d, $^1J_{PC}$ = 131.1 Hz, P=C), 49.08 and 52.88 (2O*C*H_3), 58.96 (d, $^2J_{PC}$ = 18.3 Hz, P-C-*C*H), 126.71 (d, $^1J_{PC}$ = 91.7 Hz, C_{ipso}), 128.87 (d, $^3J_{PC}$ = 10.7 Hz, C_{meta}), 132.19 (C_{para}), 133.60 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 170.29 (d, $^3J_{PC}$ = 12.3 Hz, C=O), 170.59 (d, $^2J_{PC}$ = 17.6 Hz, P-C=*C*), 171.39 (1C, CH_2-*C*O), 172.01 (1C, S-*C*O); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 22.68 (Ph_3P^+-C).

Minor rotamer *E*-4e (37%)

^{1}H NMR (500.1 MHz, $CDCl_3$), δ_H 3.58 and 3.69 (6H, 2s, 2OCH_3), 3.73 (2H, dd, $^2J_{HH}$ = 16.1, S-CH_2), 4.81 (1H, d, $^3J_{PH}$ = 15.9 Hz, P-C-*CH*), 7.45-7.70 (15H_{arom}, m, 3C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 32.74 (1C, S-*C*H_2), 38.15 (d, $^1J_{PC}$ = 137.0 Hz, P=C), 50.53 and 52.64 (2 O*C*H_3), 58.54 (d, $^2J_{PC}$ = 17.6 Hz, P-C-*C*H), 126.05 (d, $^1J_{PC}$ = 91.7 Hz, C_{ipso}), 128.51 (d, $^3J_{PC}$ = 12.1 Hz, C_{meta}), 132.16 (C_{para}), 133.64 (d, $^2J_{PC}$ = 9.7 Hz, C_{ortho}), 170.46 (d, $^3J_{PC}$ = 17.5 Hz, C=O), 171.01 (d, $^2J_{PC}$ = 18.7 Hz, P-C=*C*), 171.27 (1C, CH_2-*C*O), 172.05 (1C, S-*C*O); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 22.52 (Ph_3P^+-C).

Diethyl -2-(2,4-thiazolidinedione-2-yl)- 3-(triphenylphosphanylidene) butaned- ioate (**4f**).

White crystals, m.p. 134-136 ºC, 0.49g, yield 91%; IR (í$_{max}$, cm^{-1}): 1740, 1715, 1680 and 1636 (C=O). MS, (m/z, %): 391 (M-2CO_2Et, 53), 275 (M-PPh_3, 74), 262 (PPh_3, 74), 183 (PPh_2, 75), 108 (PPh, 37). Anal. calcd. for $C_{29}H_{28}NO_6PS$ (549): C, 63.36; H, 5.14; N, 2.55 %. Found: C, 63.30; H, 5.21; N, 2.49%.

Major rotamer *Z*-4f (71%)

^{1}H NMR (500.1 MHz, $CDCl_3$), δ_H 0.44 and 1.26 (6H, 2t, $^3J_{HH}$ = 6.8 Hz 2OCH_2CH_3), 3.68 (2H, dd, $^2J_{HH}$ = 16.5 Hz, S-CH_2), 3.76 and 4.14 (4H, 2m, 2ABX$_3$systhem 2OCH_2CH_3), 4.79 (1H, d, $^3J_{PH}$ = 15.9 Hz, P-C-C*H*), 7.48-7.73 (15H_{arom}, m, 3C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 14.12 and 14.33 (2s, 2OCH_2*C*H_3), 32.97 (1C, S-*C*H_2), 36.12 (d, $^1J_{PC}$ = 130.5 Hz, P=C), 57.62 and 59.14. (2S, 2O*C*H_2CH_3), 59.78 (d, $^2J_{PC}$ = 18.2 Hz, P-C-*C*H), 126.42 (d, $^1J_{PC}$ = 91.8 Hz, C_{ipso}), 128.73 (d, $^3J_{PC}$ = 11.2 Hz, C_{meta}), 132.09 (C_{para}), 133.64 (C_{ortho}), 168.39 (d, $^3J_{PC}$ = 12.4 Hz, C=O), 169.77 (d, $^2J_{PC}$ = 11.6 Hz, P-C=C), 170.60 (1C, CH_2-*C*O), 170.67 (1C, S-*C*O); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 22.66 (Ph_3P^+-C).

Minor rotamer *E*-4f (29%)

^{1}H NMR (500.1 MHz, $CDCl_3$), δ_H 1.18 and 1.30 (6H, 2t, $^3J_{HH}$ = 7.2 Hz, 2OCH_2CH_3), 3.74 (2H, dd, $^2J_{HH}$ = 16.3 Hz, S-CH_2), 4.04 and 4.24 (4H, 2m, 2ABX$_3$systhem 2OCH_2CH_3), 4.77 (1H, d, $^3J_{PH}$ = 18.0 Hz, P-C-C*H*), 7.48-7.73 (15H_{arom}, m, 3C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 13.88 and 13.91 (2s, 2OCH_2*C*H_3), 32.86 (1C, S-*C*H_2), 38.04 (d, $^1J_{PC}$ = 138.8 Hz, P=C), 57.67 and 59.36 (2s, 2O*C*H_2CH_3), 59.94 (d, $^2J_{PC}$ = 17.0 Hz, P-C-*C*H), 126.37 (d, $^1J_{PC}$ = 92.1 Hz, C_{ipso}), 128.50 (d, $^3J_{PC}$ = 12.1 Hz, C_{meta}), 132.14 (C_{para}), 133.60 (C_{ortho}), 168.48 (d, $^3J_{PC}$ = 12.7 Hz, C=O), 169.67 (d, $^2J_{PC}$ = 14.8 Hz, P-C=C), 170.45 (1C, CH_2-*C*O), 170.85 (1C, S-*C*O); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 22.71 (Ph_3P^+-C).

Di-tert-buthyl-2-(2,4-thiazolidinedione-1-yl)-3-(triphenylphosphanylidene) butanedioate (**4g**)

White crystals, m.p. 133-135 ºC, 0.58g, yield 96%; IR (ímax, cm-1): 1737, 1729, 1665 and 1639 (C=O).). MS, (m/z, %): 343 (M-PPh_3, 9), 276 (M-PPh_2 and 2OCMe_3,38), 262 (PPh_3, 75), 227 (M-PPh_3 and $C_3H_2O_2NS$, 6), 183 (PPh_2, 63), 108 (PPh, 26). Anal. calcd. for $C_{33}H_{36}NO_6PS$ (605): C, 65.42; H, 5.99; N, 2.31 %. Found: C, 65.51; H, 6.05; N, 2.35%.

Major rotamer *Z*-4g

1H NMR (500.1 MHz, $CDCl_3$), δ_H 0.94 and 1.54 (18H, 2s, 2OC*Me*3), 3.72 (2H, dd, $^2J_{HH}$ = 16.9 Hz, S-CH_2), 4.62 (1H, d, $^3J_{PH}$ = 17.3 Hz, P-C-C*H*), 7.48-7.75 (15H_{arom}, m, 3C_6H_5); ^{13}C NMR (125.8 MHz, $CDCl_3$), δ_C 28.32 and 28.37 (2OC*Me*$_3$), 32.82 (1C, S-*C*H_2), 36.13 (d, $^1J_{PC}$ = 130.8 Hz, P=C), 60.54 (d, $^2J_{PC}$ = 17.9 Hz, P-C-*C*H), 77.17 and 81.26 (2s, 2O*C*Me_3), 127.51 (d, $^1J_{PC}$ = 91.7 Hz, C_{ipso}), 128.64 (d, $^3J_{PC}$ = 11.7 Hz, C_{meta}), 132.01(C_{para}), 133.64 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 167.68 (d, $^3J_{PC}$ = 12.6 Hz, C=O), 168.66 (d, $^2J_{PC}$=13.3 Hz, P-C=C), 169.82 (1C, CH_2-*C*O), 170.74 (1C, S-*C*O); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.15 (Ph_3P^+-C).

Dimethyl 2-(rhodanine-1-yl)-3-(triphenylphosphanylidene) butanedioate (4h)

White crystals, m.p 108-110 °C, 0.48 g , yield 90 % . IR (KBr) (v_{max}, cm^{-1}): 1722, 1747 and 1623 (C=O). MS, (m/z, %): 537 (M^+, 6), 475 (M-2OCH_3, 52), 419 (M-2CO_2CH_3, 36), 262 (PPh_3, 85), 183 (PPh_2, 61), 120 ($C_3H_2NOS_2$, 29), 108 (PPh, 44), Anal. calcd. for $C_{27}H_{24}NO_5PS_2$ (537): C, 60.31;

H, 4.50; N, 2.67 %. Found: C, 60.25; H, 4.58; N, 2.75%.

Major isomer *Z*-4h (66%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.07 and 3.69 (6H, 2s, $2OCH_3$), 3.83 (2H, s, S-CH_2), 5.39 (1H, d, $^3J_{PH}$ = 14.4 Hz, P=C-C*H*), 7.47-7.72 (15Haro, m, $3C_6H_5$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 33.90 (1C, S-*C*H$_2$), 43.50 (d, $^1J_{PC}$ = 126.2 Hz, P=*C*), 49.34 and 52.30 (2s, $2OCH_3$), 63.25 (d, $^2J_{PC}$ = 15.7 Hz, P-C-*C*H), 126.30 (d, $^1J_{PC}$ = 92.1 Hz, C_{ipso}), 128.57 (d, $^3J_{PC}$ = 12.2 Hz, C_{meta}), 132.01 (d, $^4J_{PC}$ = 2.2 Hz, C_{para}), 133.47 (d, $^2J_{PC}$ = 8.9 Hz, C_{ortho}), 165.4 (C=O), 170.60 (1C, CH_2-*C*O), 170.69 (1C, S-*C*S); 171.59 (d, $^2J_{PC}$ = 12.5 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.50 (Ph_3P^+-C).

Minor isomer *E*-4h

(34%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.60 and 3.71 (6H, 2s, $2OCH_3$), 3.81 (2H, s, S-CH_2), 5.51 (1H, d, $^3J_{PH}$ = 17.4 Hz, P=C-C*H*), 7.47-7.72 (15Haro, m, $3C_6H_5$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 33.97 (1C, S-*C*H$_2$), 45.09 (d, $^1J_{PC}$ =137.3 Hz, P=C), 51.36 and 52.47 (2s, $2OCH_3$), 63.78 (d, $^2J_{PC}$ = 15.9 Hz, P-C-*C*H), 125.86 (d, $^1J_{PC}$=92.0 Hz, C_{ipso}), 128.90 (d, $^3J_{PC}$ = 12.0 Hz, C_{meta}), 132.29 (d, $^4J_{PC}$ = 2.4 Hz, C_{para}), 133.59 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 165.7 (C=O), 169.83 (d, $^2J_{PC}$ = 12.3 Hz, P-C=*C*). 170.96 (1C, CH_2-*C*O), 171.16 (1C, S-*C*S); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.42 (Ph_3P^+-C).

Di-tert-butyl 2-(rhodanine-1-yl)-3-(triphenylphosphanylidene) butanedioate (4i)

White crystals, m.p 157-159 ºC, 0.58 g, yield 93 % . IR (ν_{max}, cm^{-1}): 1726, 1638 (C=O). MS, (m/z, %): 621 (M^+, 5), 507 (M-2CMe_3, 34), 475 (M^+-2OCMe_3, 49), 262 (PPh_3, 85), 183 (PPh_2, 60), 108 (PPh, 51), Anal. calcd. for $C_{33}H_{36}NO_5PS_2$ (621): C, 63.74; H, 5.84; N, 2.30 %. Found: C, 63.80; H, 5.91; N, 2.26%.

Major isomer *Z*-4i (87%)

^{1}H NMR (500.1 MHz, $CDCl_3$), δ 1.28 and 1.39 (18H, 2s, 2C*Me*$_3$), 3.73 (2H, d, S-CH_2), 4.63 (1H, d, $^3J_{PH}$ = 16.6 Hz, P-C-C*H*), 7.27-7.73 (15Haro, m, $3C_6H_5$). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ 28.25 and 28.48 (2s, 2C*Me*$_3$), 34.12 (1C, S-*C*H$_2$), 40.92 (d, $^1J_{PC}$ =126.9 Hz, P=*C*), 64.33 (d, $^2J_{PC}$ = 14.7 Hz, P-C-*C*H), 77.92 and 80.43 (2s, 2O*C*Me$_3$), 127.84 (d, $^1J_{PC}$ = 91. 6 Hz, C_{ipso}), 128.31 (d, $^3J_{PC}$ = 12.2 Hz, C_{meta}), 131.70 (C_{para}), 133.99 (d, $^2J_{PC}$ = 9.7 Hz, C_{ortho}), 167.85 (d, $^3J_{PC}$ =12.2 Hz, C=O), 170.06 (d, $^2J_{PC}$ =13.8 Hz, P-C=*C*). 171.63 (1C, CH_2-*C*O), 171.97 (1C, S-*C*S); ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 22.09 (Ph_3P^+-C).

Dimetyl-2-(4,5,6,7-tetrahydroindazole-1-yl)-3-(triphenylphosphanylidene) butanedioate (4j)

White crystals, m.p 154-156°C, 0.45 g, yield 87 % . IR(KBr) (ν_{max}, cm^{-1}): 1753 and 1636 (2C=O). MS (m/z, %): 526 (M^+, 6), 501 (M^+-CO_2Me, 7), 467 (M^+-CO_2CH_3,100), 405(M^+-$C_7H_9N_2$,65), 262 (PPh_3, 80), 183 (PPh_2, 100), 108 (PPh, 40), 77 (Ph, 15), 59 (CO_2Me, 7). Anal. calcd. for $C_{31}H_{31}N_2O_5P$ (526): C, 70.69; H, 5.94; N, 5.32 %. Found: C, 70.63; H, 5.98; N, 5.38%.

Major isomer *Z*-4j (52%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.73 and 2.68 (8H, m, 4CH_2), 3.14 and 3.72 (6H, 2s, $2OCH_3$), 4.90 (1H, d, $^3J_{PH}$ = 16.7 Hz, P=C-C*H*), 7.45-7.72 (16Haro, m, $3C_6H_5$ and $C_7H_9N_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$): 20.87, 23.23 and 23.54 (4 CH_2), 43.72 (d, $^1J_{PC}$ = 128.2 Hz, P=C), 49.26 and 52.35 (2s, $2OCH_3$), 64.54 (d, $^2J_{PC}$ = 15.0 Hz, P=C-*C*H), 115.45 (1C, N-C=*C*), 126.44 (d, $^1J_{PC}$ = 92.9 Hz, C_{ipso}), 128.49 (d, $^3J_{PC}$ = 12.1 Hz, C_{meta}), 131.92 (C_{para}), 133.40 (1C, N-N=C), 133.64 (d, $^2J_{PC}$ = 9.9 Hz, C_{ortho}), 146.90 (1C, N-*C*=C), 165.37 (C=O), 172.59 (d, $^2J_{PC}$ = 13.0 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.18 (Ph_3P^+-C).

Minor isomer *E*-4j (48%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.73 and 2.68 (8H, m, 4CH_2), 3.61 and 3.72 (6H, 2s, $2OCH_3$), 4.93 (1H, d, $^3J_{PH}$ = 18.3 Hz, P=C-C*H*), 7.45-7.72 (16H, m, $3C_6H_5$ and $C_7H_9N_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$): 21.94, 22.90 and 23.63 (4 CH_2), 43.94 (d, $^1J_{PC}$ = 133.8 Hz, P=C), 52.22 and 52.53 (2s, $2OCH_3$), 63.93 (d, $^2J_{PC}$ = 16.3 Hz, P=C-*C*H), 115.13 (1C, N-*C*=C), 125.93 (d, $^1J_{PC}$ = 82.4 Hz, C_{ipso}), 128.81 (d, $^3J_{PC}$ = 12.3 Hz, C_{meta}), 131.92 (C_{para}), 133.19 (1C, N-N=C), 133.64 (d, $^2J_{PC}$ = 9.9 Hz, C_{ortho}), 147.43 (1C, N-*C*=C), 165.68 (C=O), 169.78 (d, $^2J_{PC}$ = 12.1 Hz, P-C=*C*), ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.06 (Ph_3P^+-C).

Dimethyl 2-(3-methylpyrazole-1-yl)-3-(triphenylphosphanylidene) butanedioate (4k)

White powder, m.p 183-144°C, 0.46 g, yield 94%, IR (ν_{max}, cm^{-1}): 1755 and 1638 (C=O).

MS (m/z, %): 486 (M^+, 9), 423 (M^+-CO_2Me, 100), 405 (M^+-$C_4H_5N_2$, 22), 262 (PPh_3, 35), 183 (PPh_2, 50), 108 (PPh, 20), 77 (Ph, 8). Anal. calcd. for $C_{28}H_{27}N_2O_4P$ (486): C, 69.11; H, 5.60; N, 5.76 %. Found: C, 68.97; H, 5.65; N, 5.80 %.

Major isomer *Z*-4k (55%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.17 (3H, s, CH_3), 3.20 and 3.72 (6H, 2s, $2OCH_3$), 4.91 (1H, d, $^3J_{PH}$ = 16.6 Hz, P=C-C*H*), 7.28-7.95 (17Haro, m, $3C_6H_5$ and $C_4H_5N_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.52 (s, CH_3), 43.76 (d, $^1J_{PC}$ = 127.7 Hz, P=*C*), 49.34 and 52.30 (2s, $2OCH_3$), 64.52 (d, $^2J_{PC}$ = 15.9 Hz, P-C-*C*H), 104.97 (1C, $C_4H_5N_2$), 126.30 (d, $^1J_{PC}$ = 92.1 Hz, C_{ipso}), 128.57 (d, $^3J_{PC}$ = 12.2 Hz, C_{meta}), 132.01 (d, $^4J_{PC}$ = 2.2 Hz, C_{para}), 132.13 (1C, $C_4H_4N_2$), 133.47 (d, $^2J_{PC}$ = 8.9 Hz, C_{ortho}), 146.50 (N-N=C), 165.4 (C=O), 172.50 (d, $^2J_{PC}$ =12.6 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.08 (Ph_3P^+-C).

Minor isomer *E*-4k (45%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 2.20 (3H, s, CH_3), 3.61 and 3.71(6H, 2s, $2OCH_3$), 4.95 (1H, d, $^3J_{PH}$ = 18.2 Hz, P=C-C*H*), 7.28-7.95 (17Haro, m, $3C_6H_5$ and $C_4H_5N_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 11,98 (s, CH_3), 44.04 (d, $^1J_{PC}$ = 138.0 Hz, P=C), 50.32 and 52.32 (2s, $2OCH_3$), 63.57 (d, $^2J_{PC}$ = 15.8 Hz, P-C-*C*H), 104.77 (1C, $C_4H_5N_2$), 125.67 (d, $^1J_{PC}$ = 92.2 Hz, C_{ipso}), 128.84 (d, $^3J_{PC}$ = 12.1 Hz, C_{meta}), 132.13 (1C, $C_4H_5N_2$), 132.29 (d, $^4J_{PC}$ = 2.4 Hz, C_{para}), 133.59 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 147.00 (N-N=C), 165.7 (C=O), 169.83 (d, $^2J_{PC}$ = 12.3 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.84 (Ph_3P^+-C).

Diethyl 2-(3-methylpyrazole-1-yl)-3-(triphenylphosphanylidene) butanedioate (4l).

white crystals, m.p 147-149°C, 0.47 g , yield 92% . IR(KBr) (ν_{max}, cm^{-1}): 1757 and 1635 (C=O). MS (m/z, %): 514 (M^+, 3), 441 (M^+-CO_2Et, 100), 262 (PPh_3, 42), 183 (PPh_2, 44), 108 (PPh, 21), 77 (Ph, 8). Anal. calcd. for $C_{30}H_{31}N_2O_4P$ (514): C, 70.00; H, 6.08; N, 5.44 %. Found: C, 70.38; H, 6.13; N, 5.49 %.

Major isomer *Z*-4l (63%): ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 0.48 and 1.23 (6H, 2t, $^3J_{HH}$ = 7.1Hz, $2OCH_2CH_3$), 2.17 (3H, s, CH_3), 3.75 and 4.10 (4H, 2m, $2ABX_3$ system, $2OCH_2CH_3$), 4.90 (1H, d, $^3J_{PH}$ = 16.8 Hz, P-C-C*H*), 7.20-7.97 (17Haro, m, $3C_6H_5$ and $C_4H_5N_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$): 13.56 (s, CH_3) 13.56 and 14.21 ($2OCH_2CH_3$), 43.40 (d, $^1J_{PC}$ = 127.6 Hz, P=*C*), 57.75 and 61.09 (2s, $2OCH_2CH_3$), 64.53 (d, $^2J_{PC}$ = 16.6 Hz, P-C-*C*H), 104.80 (1C, $C_4H_5N_2$), 126.62 (d, $^1J_{PC}$ = 92.1 Hz, C_{ipso}), 128.70 (d, $^3J_{PC}$ = 12.1 Hz, C_{meta}), 132.21 (C_{para}), 133.61 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 133.67 (1C, $C_4H_5N_2$), 146.13 (1C, N-N=C), 169.21 (d, $^3J_{PC}$ = 12.8 Hz,C=O), 171.68 (d, $^2J_{PC}$ = 12.3 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.09 (Ph_3P^+-C).

Minor isomer *E*-4l (37%)

^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.18 and 1.30 (6H, 2t, $^3J_{HH}$=7.1 Hz, $2OCH_2CH_3$), 2.20 (3H, s, CH_3), 4.75 and 4.20 (4H, 2m, $2ABX_3$system, $2OCH_2CH_3$), 4.91 (1H, d, $^3J_{PH}$ = 18.1 Hz, P-C-C*H*), 7.20-7.97 (17Haro, m, $3C_6H_5$ and $C_4H_5N_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$): 13.11 (s, CH_3), 13.99 and 14.84 ($2OCH_2CH_3$), 43.85 (d, $^1J_{PC}$ = 135.6 Hz, P=C), 58.39 and 61.09 (2s, $2OCH_2CH_3$), 63.86 (d, $^2J_{PC}$ = 16.3 Hz, P-C-*C*H), 104.64 (1C, $C_4H_5N_2$), 125.96 (d, $^1J_{PC}$ = 92.7 Hz, C_{ipso}), 128.70 (d, $^3J_{PC}$ = 12.1 Hz, C_{meta}), 132.21 (C_{para}), 133.61 (d, $^2J_{PC}$ = 9.8 Hz, C_{ortho}), 133.67 (1C, $C_4H_5N_2$), 146.61 (1C, N-N=C), 169.99 (d, $^3J_{PC}$ = 12.8 Hz,C=O), 171.53 (d, $^2J_{PC}$ = 10.6 Hz, P-C=C). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24. 95 (Ph_3P^+-C).

Di-tert-butyl 2-(3-methylpyrazole-1-yl)-3-(triphenylphosphanylidene) butanedioate (4m).

White crystals, m.p 175-177 ºC, 0.55 g, yield 96% . IR (ν_{max}, cm^{-1}): 1749, 1642 (C=O). MS, (m/z, %): 570 (M^+, 10), 469 (M^+-CO_2CMe_3, 65), 287 (M^+- PPh_3-C-CH,85), 262 (PPh_3, 50), 183 (PPh_2, 55), 108 (PPh, 23), 77 (Ph, 5), 57 (CMe_3, 33). Anal. calcd. for $C_{34}H_{39}N_2O_4P$ (570): C, 71.54; H, 6.89; N, 4.91 %. Found: C, 71.60; H, 6.92; N, 4.89 %.

Major isomer *Z*-4m (57%)

^{1}H NMR (500.1 MHz, $CDCl_3$), δ 0.95 and 1.50 (18H, 2s, $2CMe_3$), 2.15 (3H, s, CH_3), 4.96 (1H, d, $^3J_{PH}$ = 17.3 Hz, P-C-C*H*), 6.60-8.00 (17Haro, m, $3C_6H_5$ and $C_4H_5N_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ 13.56 (s, CH_3), 28.18 and 28.37 (2s, $2CMe_3$), 43.21 (d, $^1J_{PC}$ = 127.1 Hz, P=*C*), 65.24 (d, $^2J_{PC}$ = 16.74 Hz, P-C-*C*H), 77.89 and 80.54 (2s, $2OCMe_3$), 104.68 (1C, $C_4H_5N_2$), 127.4 (d, $^1J_{PC}$ = 92.0 Hz, C_{ipso}), 128.51 (d, $^3J_{PC}$ = 12.3 Hz, C_{meta}), 132.00 (C_{para}), 133.71 (d, $^2J_{PC}$ = 9.6 Hz, C_{ortho}), 145.85 (1C, $C_4H_5N_2$), 168.65 (d, $^3J_{PC}$ = 12.2 Hz, C=O), 170.39 (d, $^2J_{PC}$ = 13.3 Hz, P-C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.91 (Ph_3P^+-C).

Minor isomer *E*-4m (43%)

^{1}H NMR (500.1 MHz, $CDCl_3$), δ 1.46 and 1.48 (18H, 2s, 2C*Me*$_3$), 2.18 (3H, s, CH_3), 4.99 (1H, d, $^{3}J_{PH}$ = 16.9 Hz, P-C-C*H*), 6.60-8.00 (17Haro, m, $3C_6H_5$ and $C_4H_5N_2$). ^{13}C NMR (125.8 MHz, $CDCl_3$), δ 11.01 (s, CH_3), 28.12 and 28.45 (2s, 2C*Me*$_3$), 43.55 (d, $^{1}J_{PC}$ = 138.1 Hz, P=*C*), 64.20 (d, $^{2}J_{PC}$ =15.08 Hz, P-C-*C*H), 77.93 and 80.42 (2s, 2O*C*Me$_3$), 104.39 (1C, $C_4H_5N_2$), 127.27 (d, $^{1}J_{PC}$ = 92.1 Hz, C_{ipso}), 128.51 (d, $^{3}J_{PC}$ = 12.3 Hz, C_{meta}), 132.00 (C_{para}), 133.93 (d, $^{2}J_{PC}$ = 9.8 Hz, C_{ortho}), 146.41 (1C, $C_4H_5N_2$), 168.65 (d, $^{3}J_{PC}$ = 12.2 Hz, C=O), 170.39 (d, $^{2}J_{PC}$ = 13.3 Hz,P-C=C). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.47(Ph_3P^{+}-C).

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