Synthesis of functionalised phosphonates or phosphoranes by reaction between trialkyl phosphites or triphenylphosphine, dimethyl acetylenedicarboxylate and aldehyde ethyl carbazones

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Protonation of the reactive intermediate produced from the reaction between trialkyl phosphites and dimethyl acetylenedicarboxylate by ethyl carbazones of aromatic aldehydes following by conjugate addition of the anion of ethyl carbazone on the phosphonium salt intermediate leads to functionalised phosphonates in good yields. Triphenylphosphine also reacted with dimethyl acetylenedicarboxylate and ethyl carbazones to produce functionalised phosphoranes in good yields.

Keywords: dimethyl acetylenedicarboxylate, trialkyl phosphites, ethyl carbazones, phosphonates, stereoselective synthesis

Organophosphorus compounds, those bearing a carbon atom bound directly to a phosphorus atom, are synthetic targets of interest, at least because of their value for a variety of industrial, biological and chemical synthetic uses.[1-3] Reaction between phosphites and acetylene diesters in the presence of an acidic organic compound is known to produce phosphite ylides as the intermediate or the final product.[4-8] We recently reported the reaction between trimethyl phosphite, dimethyl acetylenedicarboxylate (DMAD) and aldehyde semicarbazones forming phosphonate derivatives **1** (Fig. 1).[5] When tributyl phosphite was used, phosphite ylides **2** were isolated as stable crystalline solids.[6] Three-component reaction of aldehyde semicarbazones, DMAD and triphenylphosphine has been reported to produce phosphoranes **3**.[7] Similar phosphorus ylides **4** were obtained from the reaction of benzoylhydrazones of aldehydes, DMAD and triphenylphosphine,[8] but no product was isolated from the reaction of trialkyl phosphites, DMAD and benzoylhydrazones.

In continuation of our work on the reaction between trivalent phosphorus nucleophiles and acetylene diesters in the presence of organic NH, OH, or CH-acids,[5-12] we here report the results of our study on the reaction between DMAD and trialkyl phosphites or triphenylphosphine in the presence of ethyl carbazones of aromatic aldehydes. Thus, the reaction of DMAD (**6**) with trialkyl phosphite **7** in the presence of ethyl carbazone **5** leads to the corresponding phosphonate **8** in fairly high yields (Scheme 1).

Products **8a–g** were all new compounds and their structures were deduced from their elemental analyses and spectral data. The ^{1}H NMR spectrum of compound **8a** displayed signals at 1.39 (triplet, J = 7 H_Z), 4.35 (quartet, J = 7 H_Z), 4.03 (dd, $^3J_{HH}$ = 11 H_Z, $^2J_{HP}$ = 20 H_Z) and 5.73 ppm (dd, $^3J_{HH}$ = 11 H_Z,

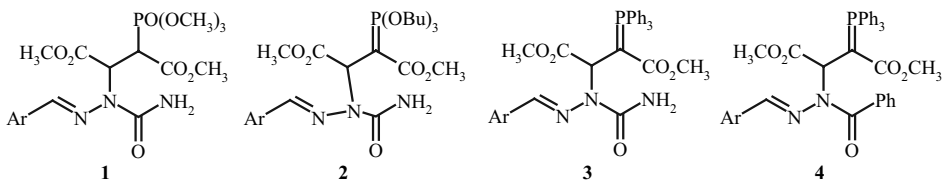
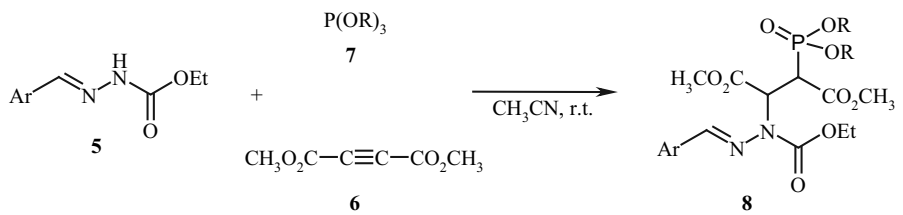


Fig. 1



8	Ar	R	%Yield
a	phenyl	Me	89
b	*p*-CH_3O-phenyl	Me	90
c	*m*-CH_3O-phenyl	Me	91
d	*m*-CH_3O-phenyl	Et	90
e	*m*-CH_3O-phenyl	Bu	91
f	*p*-Cl-phenyl	Me	88
g	*p*-Cl-phenyl	Bu	94

Scheme 1 Three-component reaction between trialkyl phosphites, DMAD and ethyl carbazones.

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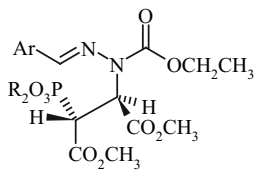
$^3J_{HP}$ = 3 H_Z) for ethoxy group and two vicinal methine groups, respectively. Two methoxy groups connected to phosphorus atom are diastereotopic and were observed as two doublets at 3.69 and 3.73 ppm ($^3J_{HP}$ = 11 H_Z). Two single signals were observed at 3.79 and 3.86 ppm for two methoxycarbonyl groups. Aromatic protons resonated between 7.41 and 7.70 ppm as multiplets. A single signal was observed at 8.87 ppm for the HC=N group.

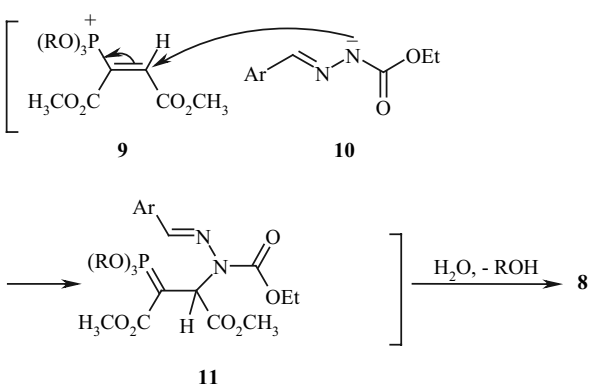
Observation of $^3J_{HH}$ = 11 Hz for the vicinal protons in compound **8a** indicates an anti arrangement for these protons.[13,14] Since compound **8a** possesses two stereogenic centres, two diastereoisomers with anti HCCH arrangements are possible (Scheme 2). The three-bond carbon-phosphorus coupling, $^3J_{CP}$, depends on configuration, as expected, transoid couplings being larger than cisoid ones. The observation of $^3J_{CP}$ of 19 Hz for the ester C=O group is in agreement with the (*2R,3S*)-**8a** and its mirror image (*2S,3R*)-**8a** geometries.[15] The same diastereomers were observed for compounds **8b–g**.

A reasonable mechanism for the formation of compounds **8** is presented in Scheme 3. The initial addition of phosphite **7** on DMAD leads to a diionic intermediate that then protonated by ethyl carbazone **5** to produce vinyl phosphonium **9**. The conjugate addition of anion **10** to cation **9** afforded the phosphite ylide **11** which then hydrolyses to product **8**.



(2*S*,3*R*) - **8**

Scheme 2 Stereochemistry of phosphonate **8**.



9 **10**

11

Scheme 3 Mechanism of formation of phosphonate **8**.

Reaction of the aldehyde ethyl carbazones with DMAD was also examined in the presence of triphenylphosphine. Treatment of DMAD with PPh_3 and ethyl carbazones lead to the formation of ylide **13** in good yields (Scheme 4).

The NMR spectra of ylides **13a–c** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial C,C double bond is slow on the NMR time scale at room temperature (Scheme 5).

The ^{1}H NMR spectrum of **13a** displays two sharp lines (δ 3.13, 3.83 ppm) for the major isomer arising from the methyl groups, along with a signal for the methine proton at 5.04, which appears as a doublet ($^3J_{HP}$ = 16 Hz). The corresponding signals for the minor isomer appear at δ 3.60, 3.77 ppm (for the methyl groups) and at δ 5.21 ppm ($^3J_{HP}$ = 14 H_Z) for the methine proton. The signals at 8.79 and 9.01 ppm, are related to CH=N protons of the two isomers. The ^{31}P NMR spectrum of compound **13a** consists of two signals at 26.2 and 25.6 for the major and the minor isomer, respectively. These shifts are similar to those observed for other stable phosphorus ylides.[16,17] The structural assignments made on the basis of the NMR spectra of compounds **13a–c** were supported by their IR spectra. The carbonyl region of the spectrum exhibits absorption bands at 1712–1743 cm^{-1} for the ester groups.

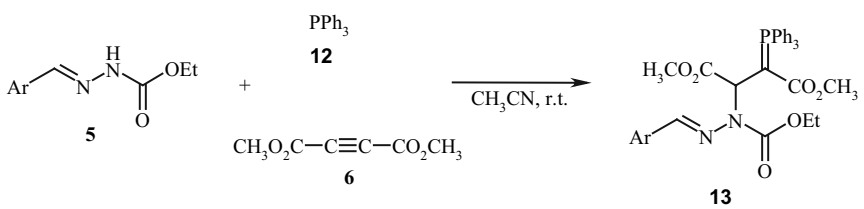
In summary, we report here that three-component reaction between trialkyl phosphites, dimethyl acetylenedicarboxylate and ethyl carbazones of aromatic aldehydes leads to functionalised phosphonates in good yields. Triphenylphosphine reacted with dimethyl acetylenedicarboxylate and ethyl carbazones to produce functionalised phosphoranes in good yields.

Experimental

All melting points are uncorrected. Elemental analyses were performed at the analytical laboratory of Islamic Azad University, Yazd branch, using a Costech ECS 4010 CHNS-O analyser. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionisation potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX-500 Avance spectrometer at 500, 128.5, and 202.5 MHz, respectively. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained on solution in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. The chemicals used in this work purchased from Fluka (Buchs, Switzerland) and were used without further purification.

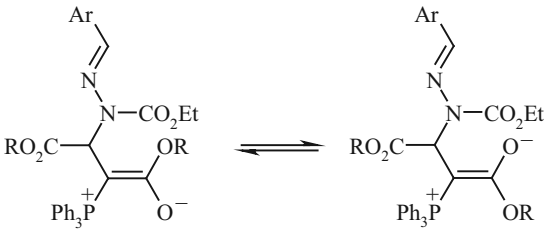
Dimethyl 2-(dimethoxyphosphoryl)-3-[2-benzylidine-1-(ethoxycarbonyl) hydrazino)]succinate **(8a):** *typical procedure for preparation of phoaphonstes* **8a–g**

To a magnetically stirred solution of trimethyl phosphite (0.25 g, 2 mmol) and benzaldehyde ethylcarbazone (0.38 g, 2 mmol) in acetonitrile (15 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in acetonitrile (3 mL) at room temperature over 2 min. The reaction mixture was then stirred



13	Ar	%Yield
a	phenyl	92
b	p-CH_3O-phenyl	94
c	p-Cl-phenyl	87

Scheme 4 Reaction between PPh_3, DMAD and ethyl carbazones.



(*E*)-**13** (*Z*)-**13**

Scheme 5 Two conformers of phosphorane **13.**

for 24 h. The solvent was removed under reduced pressure and the residue was purified by silica gel (Merck silica gel 60, 230–400 mesh) column chromatography using hexane–ethyl acetate mixture as eluent. The solvent was removed under reduced pressure to afford the product.

Yellow oil. IR (KBr)(ν_{max}, cm^{-1}): 3445 (NH), 1743, 1696 (C=O, ester). Anal. Calcd for $C_{18}H_{25}N_2O_9P$: C, 48.65; H, 5.67; N, 6.30. Found: C, 48.74; H, 5.77; N, 6.43%. MS (*m/z*, %): 444 (M^+, 8). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.69 and 3.73 (6 H, d $^3J_{PH}$ = 11 Hz, $2POCH_3$), 3.79 and 3.86 (6 H, 2 s, 2 OCH_3), 4.03 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^2J_{HP}$ = 20 H_Z, CHP), 4.35 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.73 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^3J_{HP}$ = 3 H_Z, CHN), 7.41–7.70 (5 H, m, 5 CH aromatic), 8.87 (1H, s, CH=N).^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.9 (CH_3), 31.6 (d, $^2J_{CP}$ = 3 H_Z, CH), 42.0 (d, $^1J_{CP}$ = 130 H_Z, CH), 53.4 and 53.5 (2 OCH_3), 53.8 and 53.9 (2 d, $^2J_{CP}$ = 6 H_Z, $2POCH_3$), 63.2 (OCH_2), 127.9, 128.0, 129.1, 130.8 (aromatic), 154.6 (C=N), 161.6 (C=O), 168.4 (d, $^2J_{CP}$ = 6 H_Z, C=O), 171.9 (d, $^3J_{CP}$ = 19 H_Z, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 21.51.

Dimethyl 2-(dimethoxyphosphoryl)-3-[2-(4-methoxybenzylidine)-1-(ethoxycarbonyl)hydrazino)]succinate **(8b):** Yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 3448 (NH), 1733, 1701 (C=O, ester). Anal. Calcd for $C_{19}H_{27}N_2O_{10}P$: C, 48.10; H, 5.74; N, 5.91. Found: C, 48.28; H, 5.70; N, 5.74%. MS (*m/z*, %): 474 (M^+, 6). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.28 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.67 and 3.70 (6 H, d $^3J_{PH}$ = 11 Hz, $2POCH_3$), 3.74, 3.76 and 3.82 (9 H, 3 s, 3 OCH_3), 4.00 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^2J_{HP}$ = 20 H_Z, CHP), 4.24 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.61 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^3J_{HP}$ = 3 H_Z, CHN), 6.83–7.55 (4 H, m, 4 CH aromatic), 8.81 (1H, s, CH=N).^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.8 (CH_3), 31.4 (d, $^2J_{CP}$ = 3 H_Z, CH), 40.3 (d, $^1J_{CP}$ = 130 H_Z, CH), 53.2 and 53.3 (2 OCH_3), 53.7 and 53.9 (2 d, $^2J_{CP}$ = 6 H_Z, $2POCH_3$), 55.6 (OCH_3), 63.1 (OCH_2), 129.0, 129.6, 132.3, 136.4 (aromatic), 154.8 (C=N), 161.9 (C=O), 168.7 (d, $^2J_{CP}$ = 6 H_Z, C=O), 171.7 (d, $^3J_{CP}$ = 19 H_Z, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 21.18.

Dimethyl 2-(dimethoxyphosphoryl)-3-[2-(3-methoxybenzylidine)-1-(ethoxycarbonyl)hydrazino)]succinate **(8c):** Yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 3445 (NH), 1733, 1708 (C=O, ester). Anal. Calcd for $C_{19}H_{27}N_2O_{10}P$: C, 48.10; H, 5.74; N, 5.91. Found: C, 47.85; H, 5.82; N, 6.12%. MS (*m/z*, %): 474 (M^+, 6). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.39 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.71 and 3.74 (6 H, d $^3J_{PH}$ = 11 Hz, $2POCH_3$), 3.76, 3.86 and 3.87 (9 H, 3 s, 3 OCH_3), 4.02 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^2J_{HP}$ = 20 H_Z, CHP), 4.35 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.71 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^3J_{HP}$ = 3 H_Z, CHN), 6.96–7.34 (4 H, m, 4 CH aromatic), 8.73 (1H, s, CH=N).^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.9 (CH_3), 31.8 (d, $^2J_{CP}$ = 3 H_Z, CH), 41.8 (d, $^1J_{CP}$ = 132 H_Z, CH), 53.3 and 53.4 (2 OCH_3), 53.8 and 53.9 (2 d, $^2J_{CP}$ = 6 H_Z, $2POCH_3$), 55.7 (OCH_3), 63.2 (OCH_2), 112.3, 116.9, 121.0, 130.1, 132.5, 136.7 (aromatic), 154.8 (C=N), 160.2 (C=O), 168.4 (d, $^2J_{CP}$ = 6 H_Z, C=O), 171.2 (d, $^3J_{CP}$ = 19 H_Z, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 21.37.

Dimethyl 2-(diethoxyphosphoryl)-3-[2-(3-methoxybenzylidine)-1-(ethoxycarbonyl)hydrazino)] succinate **(8d):** Yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 3450 (NH), 1730, 1698 (C=O, ester). Anal. Calcd for $C_{21}H_{31}N_2O_{10}P$: C, 50.20; H, 6.22; N, 5.58. Found: C, 50.34; H, 6.10; N, 5.43%. MS (*m/z*,%): 502 (M^+, 9). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.24, 1.37, 1.43 (9H, 3t, $^3J_{HH}$ = 7 H_Z, 3 CH_3), 3.72, 3.80 and 3.84 (9 H, 3 s, 3 OCH_3), 4.01(1 H, dd $^3J_{HH}$ = 11 H_Z, $^2J_{HP}$ = 20 H_Z, CHP), 4.09–4.32 (6 H, m,3 OCH_2), 5.68 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^3J_{HP}$ = 3 H_Z, CHN), 6.80–7.31 (4 H, m, aromatic), 8.82 (1H, s, CH=N).^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.8, 16.3 and 16.6 (3 CH_3), 31.7 (d, $^2J_{CP}$ = 3 H_Z, CH), 41.5 (d, $^1J_{CP}$ = 133 H_Z, CH), 52.6, 53.2 and 55.7 (3 OCH_3), 63.5, 66.8 and 66.9 (3 OCH_2), 112.1, 116.9, 121.1, 130.0, 132.1, 136.2 (aromatic), 154.7 (C=N), 160.2 (C=O), 168.6 (d, $^2J_{CP}$ = 6 H_Z, C=O), 172.1 (d, $^3J_{CP}$ = 19 H_Z, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 21.08.

Dimethyl 2-(dibutoxyphosphoryl)-3-[2-(3-methoxybenzylidine)-1-(ethoxycarbonyl)hydrazino)]succinate **(8e):** Yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 3438 (NH), 1731, 1697 (C=O, ester). Anal. Calcd for $C_{25}H_{39}N_2O_{10}P$: C, 53.76; H, 7.04; N, 5.02. Found: C, 53.47; H, 7.1; N, 4.88%. MS (*m/z*,%): 558 (M^+, 11). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.87, 0.95 and 1.37 (9 H, 3 t $^3J_{HH}$ = 7 H_Z, 3 CH_3), 1.29 and 1.41 (4 H, 2 sextet, 2 CH_2), 1.56 and 1.67(4 H, 2quintet, 2 CH_2), 3.73, 3.82 and 3.85 (9 H, 3 s, 3 OCH_3), 4.01–4.37 (7 H, m, 3 OCH_2 and CHP), 5.66 (1 H, dd, $^3J_{HP}$ = 7 Hz, $^3J_{HH}$ = 11 H_Z, CHN), 6.79–7.31 (4 H, m, aromatic), 8.81 (1H, s, CH=N). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.9, 14.1 and 14.8 (3 *C*H_3), 18.9 and 19.0 (2 CH_2), 31.7 (d, $^2J_{cp}$ = 3 H_Z, CHN), 32.5 and 32.8 (2 d, $^3J_{CP}$ = 7 Hz, 2 CH_2),], 41.7 (d, $^1J_{cp}$ = 130 H_Z, P-*C*), 53.2, 53.4 and 55.7 (3 O*C*H_3), 63.2 (O*C*H_2), 67.0 and 67.3 (2 d, $^2J_{cp}$ = 7 H_Z, 2 PO*C*H_2), 112.2, 116.9, 121.0, 129.9, 133.8, 136.4 (aromatic), 154.4 (C=N), 160.2 (C=O), 168.5 (d, $^2J_{CP}$ = 6 H_Z, C=O), 172.2 (d, $^3J_{CP}$ = 19 H_Z, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 20.93.

Dimethyl 2-(dimethoxyphosphoryl)-3-[2-(4-chlorobenzylidine)-1-(ethoxycarbonyl)hydrazino)]succinate **(8f):** Yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 3437 (NH), 1745, 1696 (C=O, ester). Anal. Calcd for $C_{18}H_{24}ClN_2O_9P$: C, 45.15; H, 5.05; N, 5.85. Found: C, 45.04; H, 5.13; N, 5.65%. MS (*m/z*,%): 478 (M^+, 9). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.37 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.69 and 3.72 (6 H, d $^3J_{PH}$ = 11 Hz, $2POCH_3$), 3.75 and 3.91 (6 H, 2 s, 2 OCH_3), 3.99 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^2J_{HP}$ = 20 H_Z, CHP), 4.34 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.67 (1 H, dd $^3J_{HH}$ = 11 H_Z, $^3J_{HP}$ = 3 H_Z, CHN), 7.35–7.63 (4 H, m, aromatic), 8.88 (1H, s, CH=N).^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.9 (CH_3), 31.7 (d, $^2J_{CP}$ = 3 H_Z, CHN), 42.1 (d, $^1J_{CP}$ = 132 H_Z, CH), 53.4 and 53.8 (2 OCH_3), 63.3 (OCH_2), 56.8 and 56.9 (2 d, $^2J_{CP}$ = 6 H_Z, $2POCH_3$), 129.1, 129.3, 132.2, 136.6 (aromatic), 153.9 (C=N), 161.2 (C=O), 168.3 (d, $^2J_{CP}$ = 6 H_Z, C=O), 171.9 (d, $^3J_{CP}$ = 19 H_Z, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 21.75.

Dimethyl 2-(dibutoxyphosphoryl)-3-[2-(4-chlorobenzylidine)-1-(ethoxycarbonyl)hydrazino)]succinate **(8g):** Yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 3433 (NH), 1730, 1700 (C=O, ester). Anal. Calcd for $C_{24}H_{36}ClN_2O_9P$: C, 51.20; H, 6.45; N, 4.98. Found: C, 51.37; H, 6.24; N, 5.11%. MS (*m/z*,%): 562 (M^+, 10). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.88, 0.97 and 1.38 (9 H, 3 t $^3J_{HH}$ = 7 H_Z, 3 CH_3), 1.31 and 1.43(4 H, m, 2 CH_2), 1.58 and 1.69 (4 H, m, 2 CH_2), 3.74 and 3.84 (6 H, 2 s, 2 OCH_3), 3.93–4.36 (7 H, m, 3 OCH_2 and CH P), 5.67 (1 H, dd, $^3J_{HP}$ = 7 Hz, $^3J_{HH}$ = 11 H_Z, CH N), 7.36–7.63 (4 H, m, aromatic), 8.75 (1H, s, CH=N). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 13.9, 14.0 and 14.8 (3 *C*H_3), 18.9 and 19.1 (2 CH_2), 31.6 (d, $^2J_{cp}$ = 3 H_Z, 2 CH_2), 32.7 and 32.8 (2 d, $^3J_{CP}$ = 7 Hz, 2 CH_2),], 41.5 (d, $^1J_{cp}$ = 130 H_Z, P-*C*), 53.2 and 53.4 (2 O*C*H_3), 63.2 (O*C*H_2), 66.9 and 67.2 (2 d, $^2J_{cp}$ = 7 H_Z, 2 PO*C*H_2), 129.0, 129.3, 133.6, 136.5 (aromatic), 153.1 (C=N), 161.3 (C=O), 168.5 (d, $^2J_{cp}$ = 19 Hz, C=O), 170.7 (d, $^3J_{cp}$ = 19 Hz, C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 22.09.

Dimethyl 2-(2′-Benzylidene-1-(ethoxycarbonyl)hydrazino)-3-(triphenylphosphanylidene)succinate **(13a):** *typical procedure for preparation of phosphoranes* **(13a–c):** To a magnetically stirred solution of triphenylphosphine (0.52 g, 2 mmol) and benzaldehyde ethylcarbazone (0.38 g, 2 mmol) in acetonitrile (15 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.28 g, 2 mmol) in acetonitrile (3 mL) at room temperature over 2 min. The reaction mixture was then stirred for 24 h. The solvent was evaporated at reduced pressure. The residue was precipitated in a mixture of diethyl ether–hexane. The solid was filtered and washed with diethyl ether to give the pure product.

White powder; m.p. 154–156 °C. IR (KBr) (ν_{max}, cm^{-1}): 1744, 1685, 1638 (C=O). Calcd for $C_{34}H_{33}N_2O_6P$: C, 68.45; H, 5.58; N, 4.70. Found: C, 68.22; H, 5.67; N, 4.61%. MS (*m/z*,%): 596 (M^+, 5). NMR data for the major isomer (70%), ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.08 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.13 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3), 3.98 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.04 (1 H, d, $^3J_{PH}$ = 16 H_Z,), 7.30–7.84 (20 H, m, aromatic), 8.79 (1H, s, CH=N). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.7 (CH_3), 49.5 (d, $^1J_{PC}$ = 122 H_Z, C = P), 50.7, 52.9 (2 OCH_3), 52.6 (d, $^2J_{PC}$ = 16 H_Z, CH), 61.7 (OCH_2), 126.9 (d, $^1J_{PC}$ = 91 H_Z), 128.8 ($^2J_{PC}$ = 12 H_Z), 132.3 (d, $^4J_{PC}$ = 2 H_Z), 134.1 (d, $^3J_{PC}$ = 10 H_Z), 128.9, 129.7, 134.3, 136.5 (C_6H_5), 154.5 (C=N), 161.3 (C=O), 169.5 (d, $^2J_{PC}$ = 12 H_Z, C=O), 171.6 (d, $^3J_{PC}$ = 17 H_Z C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 24.2. NMR data for the minor isomer (30%), ^{1}H NMR: δ 1.24 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.60 (3 H, s,, OCH_3), 3.77 (3 H, s, OCH_3), 4.01 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.21 (1 H, d, $^3J_{PH}$ = 14 H_Z), 7.30–7.84 (20 H, m, aromatic), 9.01 (1H, s, CH=N). ^{13}C NMR: δ 14.8 (CH_3), 49.7 (d, $^1J_{PC}$ = 122 H_Z, C = P), 50.4, 52.7 (2 OCH_3), 52.3 (d, $^2J_{PC}$ = 16 H_Z, CH), 61.9 (OCH_2), 126.5(d, $^1J_{PC}$ = 91 H_Z), 128.9 ($^2J_{PC}$ = 12 H_Z), 132.4 (d, $^4J_{PC}$ = 2 H_Z), 134.3 (d, $^3J_{PC}$ = 10 H_Z), 128.8, 129.2, 134.2, 136.4(C_6H_5),

154.2 (C=N), 161.6(C=O), 169.6 (d, $^2J_{PC}$ = 12 H_Z C=O ester), 171.1 (d, $^3J_{PC}$ = 17 H_Z C=O ester). ^{31}P NMR: δ 23.9.

Dimethyl 2-[2'-(4-methylbenzylidene)-1-(ethoxycarbonyl)hydrazino]-3-(triphenylphosphanylidene)succinate **(13b):** White powder; m.p. 172–174 °C. IR (KBr) (ν_{max}, cm^{-1}): 1752, 1681, 1630 (C=O). Calcd for $C_{35}H_{35}N_2O_7P$: C, 67.08; H, 5.63; N, 4.47. Found: C, 67.11; H, 5.63; N, 4.52%. MS (*m/z*,%): 626 (M^+, 7). NMR data for the Major isomer (69%), ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.11(3 H, s, OCH_3), 3.84 (3 H, s, OCH_3), 3.91 (3 H, s, OCH_3), 3.97 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.59 (1 H, d, $^3J_{PH}$ = 16 H_Z), 6.96–7.79 (19 H, m, aromatic), 8.70 (1H, s, CH=N). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.8 (CH_3), 49.6 (d, $^1J_{PC}$ = 122 H_Z, C = P), 50.8, 52.8, 55.8 (3 OCH_3), 52.6 (d, $^2J_{PC}$ = 15 H_Z, CH), 61.6 (OCH_2), 126.8 (d, $^1J_{PC}$ = 91 H_Z), 129.6 ($^2J_{PC}$ = 12 H_Z), 132.2 (d, $^4J_{PC}$ = 2 H_Z), 134.2 (d, $^3J_{PC}$ = 10 H_Z), 114.3, 128.9, 129.1, 146.3 (C_6H_4) 154.4 (C=N), 161.4 (C=O), 168.7 (d, $^2J_{PC}$ = 12 H_Z C=O), 170.9 (d, $^3J_{PC}$ = 17 H_Z C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 24.7. NMR data for the minor isomer (31%), ^{1}H NMR: δ 1.25 (3 H, t, $^3J_{HH}$ = 7 H_Z,CH_3), 3.57(3 H, s, OCH_3), 3.76 (3 H, s, OCH_3), 3.90 (3 H, s, OCH_3), 3.99 (2 H, q, $^3J_{HH}$ = 7 H_Z,OCH_2), 5.62 (1 H, d, $^3J_{PH}$ = 16 H_Z), 6.96–7.79 (19 H, m, aromatic), 8.88 (1H, s, CH=N). ^{13}C NMR: δ 14.7 (CH_3), 49.5 (d, $^1J_{PC}$ = 122 H_Z, C = P), 50.9, 52.9, 55.9 (3 OCH_3), 52.7 (d, $^2J_{PC}$ = 16 H_Z, CH), 61.8 (OCH_2), 126.5(d, $^1J_{PC}$ = 91 H_Z), 129.8 ($^2J_{PC}$ = 12 H_Z), 132.4(d, $^4J_{PC}$ = 2 H_Z), 134.3 (d, $^3J_{PC}$ = 10 H_Z), 114.2, 129.0, 129.6, 146.5 (C_6H_4) 154.5 (C=N), 161.3 (C=O), 168.9 (d, $^2J_{PC}$ = 12 H_Z C=O), 171.0 (d, $^3J_{PC}$ = 17 H_Z C=O). ^{31}P NMR: δ 24.2.

Dimethyl 2-[2'-(4-chlorobenzylidene)-1-(ethoxycarbonyl)hydrazino]-3-(triphenylphosphanylidene)succinate **(13c):** White powder; m.p. 165–167 °C. IR (KBr) (ν_{max}, cm^{-1}): 1735, 1687, 1635 (C=O). Calcd for $C_{34}H_{32}ClN_2O_6P$: C, 64.71; H, 5.11; N, 4.44%. Found: C, 64.82; H, 5.25; N, 4.53%. MS (*m/z*,%): 630 (M^+, 3). NMR data for the Major isomer (75%), ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.13 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3)), 4.29 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.41 (1 H, d, $^3J_{PH}$ = 16 H_Z), 7.36–7.94 (19 H, m, aromatic), 8.80 (1H, s, CH=N). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 14.9 (CH_3), 49.4 (d, $^1J_{PC}$ = 122 H_Z, C = P), 50.6, 53.0 (2 OCH_3), 52.7 (d, $^2J_{PC}$ = 16 H_Z, CH), 61.2 (OCH_2), 126.2 (d, $^1J_{PC}$ = 91 H_Z), 129.2 ($^2J_{PC}$ = 12 H_Z), 132.4 (d, $^4J_{PC}$ = 2 H_Z), 134.1 (d, $^3J_{PC}$ = 10 H_Z), 128.8, 129.0, 134.6, 135.1 (C_6H_4) 154.4 (C=N), 161.4 (C=O), 168.7 (d, $^2J_{PC}$ = 12 H_Z C=O), 170.9 (d, $^3J_{PC}$ = 17 H_Z C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 24.8. NMR data for the minor isomer (25%), ^{1}H NMR: δ 1.46 (3 H, t, $^3J_{HH}$ = 7 H_Z, CH_3), 3.60 (3 H, s, OCH_3), 3.77 (3 H, s, OCH_3)), 3.86 (2 H, q, $^3J_{HH}$ = 7 H_Z, OCH_2), 5.48 (1 H, d, $^3J_{PH}$ = 16 H_Z), 7.36–7.94 (19 H, m, aromatic), 9.01 (1H, s, CH=N).^{13}C NMR: δ 15.0 (CH_3), 49.6 (d, $^1J_{PC}$ = 122 H_Z, C = P), 50.3, 52.9 (2 OCH_3), 52.5 (d, $^2J_{PC}$ = 16 H_Z, CH), 61.4 (OCH_2), 126.5 (d, $^1J_{PC}$ = 91 H_Z), 129.1($^2J_{PC}$ = 12 H_Z), 132.1(d, $^4J_{PC}$ = 2 H_Z), 134.7 (d, $^3J_{PC}$ = 10 H_Z), 128.6, 129.2, 134.3, 135.2 (C_6H_4) 154.7 (C=N), 161.6 (C=O), 168.9 (d, $^2J_{PC}$ = 12 H_Z C=O), 171.0 (d, $^3J_{PC}$ = 17 H_Z C=O). ^{31}P NMR: δ 23.6.

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