

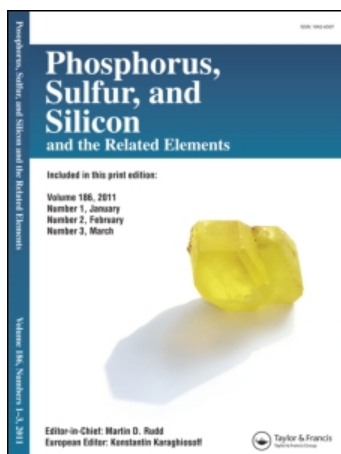
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A FACILE, ONE-POT SYNTHESIS OF AZOIC COMPOUNDS AND ANTHRAQUINONE DERIVATIVES CONTAINING DIALKYL PHOSPHORYL MOIETIES IN MULTICOMPONENT REACTIONS

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Protonation of the reactive 1:1 intermediates produced in the reactions between triphenylphosphine and dialkyl acetylenedicarboxylates by 1-amino-anthraquinone or 1,5-diphenylcarbazone as a core dye leads to vinyl phosphonium salts, which undergo Michael addition with conjugate base of NH compounds to produce stable phosphorus ylides as novel dyes in fairly good yields. These ylides can exist in two geometrical isomers (Z) and (E) for 3, because the negative charge of the ylide moiety of these compounds are strongly conjugated with the adjacent carbonyl group. Rotation around the carbon–carbon double bond is slow in the (Z) and (E) geometrical isomers on the NMR time scale at ambient temperature. These compounds are assigned by their IR, ¹H, ¹³C NMR spectral data as well as their mass spectroscopic data.

Keywords 1-Amino-anthraquinone; azoic dyes; dialkyl acetylenedicarboxylate; 1,5-diphenylcarbazone; geometrical isomers; stable phosphorus ylides

INTRODUCTION

Dyes have been the subject of much interest in recent years because of increasingly stringent restriction on the organic content of industrial effluents. Many industries (plastics, paper, textile, and cosmetics) use dyes in order to color their products. Over 100,000 commercially available dyes exist, and more than 7×10^5 tons are produced annually.^{1,2} Azoic dyes, 9,10-anthraquinone, and its derivatives constitute the largest group of commonly available dyes and pigments.^{3–5} Due to their colors, azoic dyes are used as pigments, indicators of solvent polarity, of molecular environments, and of chemical environments; they are also widely used as histological stains and in the colorimetric analysis of pharmaceuticals.^{6–11} The widespread applications of the azoic dyes as chromophoric and metallo

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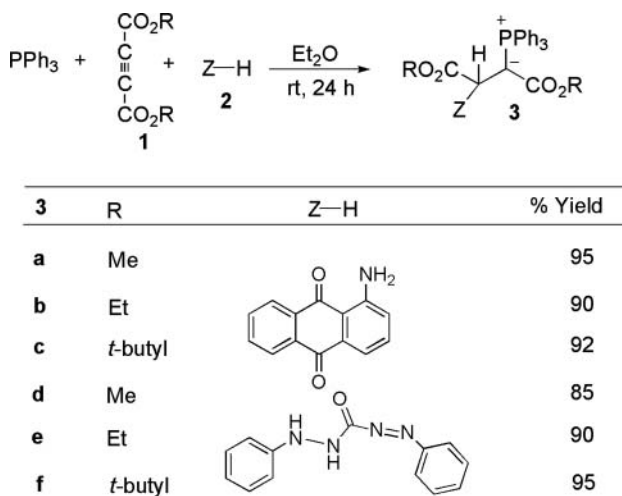
We gratefully acknowledge financial support from the Research Council of the University of Sistan and Baluchestan, Iran.

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chromic reagents,^{12–17} photochromic materials,^{18, 19} colorants,^{20, 21} nonlinear optics,^{22–25} photosensitizers,²⁶ and sensors^{27, 28} have attracted the interest of many electrochemists.^{29–33}

Amino anthraquinones are the basic structural units of disperse dyes,^{34, 35} which are an important class of dye, characterized by good fastness properties and brightness on hydrophobic fibers, such as poly(ethylene terephthalate), on which they provide mostly bright red to blue hues; also are included acylamino-anthraquinones, which furnish mainly yellow and orange dyes. In addition, anthraquinones have become recently very important due to their application in high technology electronics. Some amino anthraquinone derivatives are used in transfer printing toners, and others are used in thermal printing.^{36, 37}

In continuation of our current interest in the development of new routes to heterocyclic and carbocyclic systems,^{38–45} in this article we report a simple, one-pot synthesis of stable azo compounds and also anthraquinone derivatives containing dialkyl phosphoryl groups as novel dyes in fairly good yields (see Scheme 1).



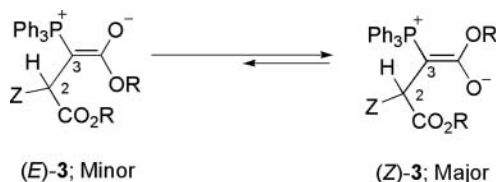
Scheme 1

RESULTS AND DISCUSSION

The reactions of 1-amino-anthraquinone or 1,5-diphenylcarbazone with dialkyl acetylenedicarboxylates **1** in the presence of triphenylphosphine were carried out in Et₂O solvent at room temperature and were finished within a few hours. The ¹H and ¹³C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **3**.

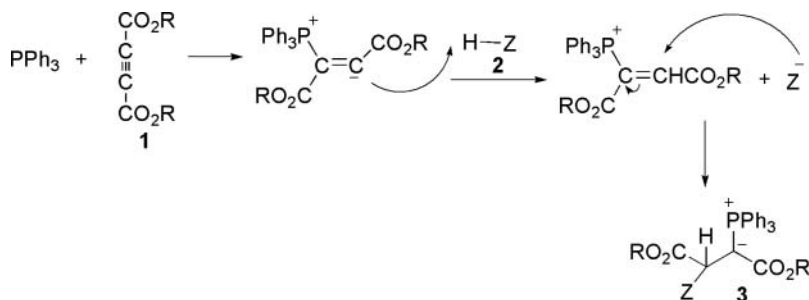
Any products other than **3** could not be detected by NMR spectroscopy. The structures of compounds **3a–f** were deduced from their IR, ¹H, ¹³C, and ³¹P NMR spectra. Their mass spectra displayed molecular ion peaks at appropriate *m/z* values. Any initial fragmentations involve the missing parts or complete loss of the side chains and scission of the ring system. The ¹H, ¹³C, and ³¹P NMR spectra of ylides **3a–f** are consistent with the presence of two isomers. The ¹H NMR spectra of **3a** showed two sharp lines (δ 3.19 and 3.73) arising from the methoxy groups in *Z*-diastereoisomer and two single sharp resonances at 3.73 and 3.82 ppm for methoxy groups in *E*-diastereoisomer. In this spectra, the characteristic methine proton appeared at 5.28 and 4.41 ppm for major and minor stereoisomers, respectively.

All of the aromatic protons resonated at δ 6.28–8.31 for major and minor isomers. The ^1H NMR spectrum of compound **3a** exhibited a N–H proton as a doublet at 10.11 ppm and a doublet at 10.33 ppm for major and minor, respectively. Other partial assignments of compound **3a** have been presented in the Experimental section. The ylide moieties of these compounds are strongly conjugated with the adjacent carbonyl group, and rotation around the partial double bond in (*E*)-**3** and (*Z*)-**3** geometrical isomers is slow on the NMR time scale at ambient temperature (see Scheme 2). Selected ^1H -, ^{13}C -, and ^{31}P NMR chemical shifts and coupling constants are shown in Table I.



Scheme 2

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,^{46–51} it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-compounds to form phosphoranes **3** (see Scheme 3).



Scheme 3

Briefly, we have prepared novel stable phosphorus ylides as a novel dyes, using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of 1-amino-anthraquinone or 1,5-diphenylcarbazone. 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. 1-Amino-anthraquinone and 1,5-diphenylcarbazone-containing phosphorus ylides **3a–f** 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 ^1H , ^{13}C , and ^{31}P NMR spectra were obtained from a Bruker DRX-500 Avance instrument with CDCl_3

Table I Selected ^1H , ^{13}C , and ^{31}P NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for H-2, OR, CO_2R , C-2, and C-3 in the major (M) and minor (m) diastereoisomers of compounds **3a–f**

Compd	Isomer%	^1H NMR spectroscopic data			^{13}C NMR data		^{31}P NMR
		H-2 ($^3J_{\text{PH}}$)	OR	CO_2R	C-2 ($^2J_{\text{PC}}$)	C-3 ($^1J_{\text{PC}}$)	
3a	M (59)	5.28 (24.0)	3.19	3.73	55.8 (12.0)	43.0 (124.9)	20.7
3a	m (41)	4.41 (18.8)	3.73	3.82	55.3 (11.8)	44.0 (135.1)	22.5
3b	M (57)	5.26 (24.1)	3.74–3.85		55.8 (13.4)	42.6 (127.5)	20.7
3b	m (43)	4.37 (18.9)	4.10–4.23		55.8 (13.4)	42.6 (127.5)	22.4
3c	M (63)	5.08 (24.8)	0.99	1.48	56.2 (13.5)	42.0 (125.0)	19.9
3c	m (37)	5.08 (24.8)	1.55	1.57	55.3 (12.7)	43.3 (124.2)	22.4
3d	M (61)	5.13 (18.5)	3.07	3.82	60.6 (17.6)	40.7 (126.2)	23.8
3d	m (39)	5.02 (16.8)	3.16	3.84	61.5 (17.1)	40.3 (126.6)	23.9
3e	M (57)	5.12 (18.4)	4.21–4.44		61.7 (17.8)	40.0 (126.8)	23.8
3e	m (43)	5.18 (18.6)	4.15–4.44		62.2 (17.7)	40.4 (126.0)	23.9
3f	M (79)	5.00 (18.3)	0.88	1.61	61.4 (17.8)	39.9 (126.3)	23.5
3f	m (21)	4.87 (18.9)	1.43	1.55	61.4 (17.8)	36.9 (126.9)	23.6

as a solvent at 500.1, 125.8, and 202.4 MHz, respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. In addition, the mass spectra were recorded on a Shimadzu GC/MS QP 1100 EX mass spectrometer operating at an ionization potential of 70 eV. Dialkyl acetylenedicarboxylates, triphenylphosphine, 1-amino-anthraquinone, and 1,5-diphenyl carbazone were purchased from Fluka and were used without further purification.

General Procedures for Preparation of Stable Phosphorus Ylides

To a magnetically stirred solution of triphenylphosphine (0.26 g, 1 mmol) and NH compound (1 mmol) in diethyl ether 10 mL, a mixture of dimethyl acetylenedicarboxylates (0.14 g, 1 mmol) in diethyl ether 3 mL was added dropwise over 10 min at room temperature. After 24 h stirring at room temperature, the product was filtered off and recrystallized from ethyl acetate.

Dimethyl-2-(*N*-1-aminoanthraquinon-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3a**).** Red powder (0.45 g), yield 95%, mp 176–179°C. IR (KBr) (λ_{max} , cm^{-1}): 1620, 1648 (2 C=O), 1730 (C=O_{ester}), 3400 (N–H). MS (m/z , %): 627 (M^+ , 1), 500 (8), 453 (53), 277 (100), 262 (13), 223 (16), 183 (26), 77 (18). Anal. Calc. for $\text{C}_{38}\text{H}_{30}\text{NO}_6\text{P}$ (627.62): C, 72.73; H, 4.78; N, 2.23%; Found: C, 73.08; H, 4.82; N, 2.15%.

Major isomer (Z)-3a (59%): ^1H NMR: 3.19 and 3.73 (6H, 2s, 2 OCH₃), 5.28 (1H, dd, $^3J_{\text{HH}} = 5.4$ Hz, $^3J_{\text{HP}} = 24.0$ Hz, P=C–CH), 6.28–8.31 (22H, m, 3 C₆H₅ and C₁₄H₉NO₂), 10.11 (1H, d, $^3J_{\text{HH}} = 6.0$ Hz, CH–NH). ^{13}C NMR: 43.0 (d, $^1J_{\text{PC}} = 124.9$ Hz, P=C), 49.4 and 52.5 (2s, 2 OCH₃), 55.8 (d, $^2J_{\text{PC}} = 12.0$ Hz, P=C–CH), 113.2, 115.5, 117.0, 118.1, 119.9, 123.5 (6C, C₁₄H₉NO₂), 126.3 (d, $^1J_{\text{PC}} = 89.5$ Hz, C_{ipso} of 3 C₆H₅), 128.5 (d, $^3J_{\text{PC}} = 12.0$ Hz, C_{meta} of 3 C₆H₅), 132.1 (C_{para} of 3 C₆H₅), 133.0, 133.2, and 133.4 (3C, C₁₄H₉NO₂), 133.7 (d, $^2J_{\text{PC}} = 9.9$ Hz, C_{ortho} of 3C₆H₅), 149.6, 150.2 and 151.4 (3C, C₁₄H₉NO₂), 170.2 (d, $^3J_{\text{PC}} = 12.7$, C=O_{ester}), 173.6 (d, $^2J_{\text{PC}} = 17.2$, P=C=C), 184.0 and 185.0 (2 C=O, C₁₄H₉NO₂). ^{31}P NMR: 20.7 (Ph₃P⁺–C).

Minor isomer (E)-3a (41%): ^1H NMR: 3.73 and 3.82 (6H, 2s, 2OCH₃), 4.41 (1H, dd, $^3J_{\text{HH}} = 6.8$ Hz, $^3J_{\text{HP}} = 18.8$ Hz, P=C–CH), 6.20–8.31 (22H, m, 3 C₆H₅ and C₁₄H₉NO₂),

10.33 (1H, d, $^3J_{\text{HH}} = 7.0$ Hz, CH–NH). ^{13}C NMR: 44.0 (d, $^1J_{\text{PC}} = 135.1$ Hz, P=C), 50.4 and 52.4 (2s, 2 OCH₃), 55.3 (d, $^2J_{\text{PC}} = 11.8$ Hz, P=C–CH), 113.2, 115.5, 117.0, 118.2, 119.9, 123.5 (6C, C₁₄H₉NO₂), 125.9 (d, $^1J_{\text{PC}} = 92.3$ Hz, C_{ipso} of 3 C₆H₅), 128.6 (d, $^3J_{\text{PC}} = 12.4$ Hz, C_{meta} of 3 C₆H₅), 132.0 (C_{para} of 3 C₆H₅), 133.0, 133.2 and 133.4 (3C, C₁₄H₉NO₂), 133.8 (d, $^2J_{\text{PC}} = 9.8$ Hz, C_{ortho} of 3 C₆H₅), 149.6, 150.1 and 151.4 (3C, C₁₄H₉NO₂), 170.2 (d, $^3J_{\text{PC}} = 12.7$, C=O_{ester}), 173.6 (d, $^2J_{\text{PC}} = 17.2$, P–C=C), 183.7 and 184.1 (2 C=O, C₁₄H₉NO₂). ^{31}P NMR: 22.5 (Ph₃P⁺–C).

Diethyl-2-(*N*-1-aminoanthraquinon-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3b). Red powder (0.45 g), yield 90%, mp 126–129°C. IR (KBr) (λ_{max} , cm^{–1}): 1620, 1664 (C=O), 1738, 1742 (C=O_{ester}), 3422 (N–H). MS (m/z , %): 655 (M⁺, 2), 485 (3), 277 (8), 223 (100), 77 (8). Anal. Calc. for C₄₀H₃₄NO₆P (655.67): C, 73.28; H, 5.19; N, 2.14%; Found: C, 73.53; H, 5.25; N, 2.20%.

Major isomer (E)-3b (57%): ^1H NMR: 0.46 and 1.28 (6H, 2t, $^3J_{\text{HH}} = 7.0$ Hz, 2OCH₂CH₃), 3.74–3.85 (4H, m, 2 ABX₃ system, 2 OCH₂CH₃), 5.26 (1H, dd, $^3J_{\text{HH}} = 5.1$ Hz, $^3J_{\text{HP}} = 24.1$ Hz, P=C–CH), 6.24–8.35 (22H, m, 3 C₆H₅ and C₁₄H₉NO₂), 10.14 (1H, d, $^3J_{\text{HH}} = 5.7$ Hz, CH–NH). ^{13}C NMR: 14.1 and 14.2 (2s, 2 OCH₂CH₃), 42.6 (d, $^1J_{\text{PC}} = 127.5$ Hz, P=C), 55.8 (d, $^2J_{\text{PC}} = 13.4$ Hz, P=C–CH), 58.0 and 61.3 (2s, 2 OCH₂CH₃), 113.2, 113.5, 115.3, 117.1, 120.1 and 123.5 (6 C, C₁₄H₉NO₂), 126.3 (d, $^1J_{\text{PC}} = 94.1$ Hz, C_{ipso} of 3 C₆H₅), 128.6 (d, $^3J_{\text{PC}} = 11.1$ Hz, C_{meta} of 3 C₆H₅), 132.0 (C_{para} of 3 C₆H₅), 132.5, 133.0 and 133.2 (3 C, C₁₄H₉NO₂), 133.8 (d, $^2J_{\text{PC}} = 9.9$ Hz, C_{ortho} of 3 C₆H₅), 149.7, 150.2 and 151.3 (3 C, C₁₄H₉NO₂), 165.0 (d, $^3J_{\text{PC}} = 12.6$ Hz, C=O_{ester}), 173.0 (d, $^2J_{\text{PC}} = 14.6$, P–C=C), 183.6 and 184.2 (2 C=O, C₁₄H₉NO₂). ^{31}P NMR: 20.7 (Ph₃P⁺–C).

Minor isomer (Z)-3b (43%): ^1H NMR: 1.21 and 1.32 (6H, 2t, $^3J_{\text{HH}} = 6.9$ Hz, 2 OCH₂CH₃), 4.10–4.23 (4H, 2m, 2ABX₃ system, 2 OCH₂CH₃), 4.37 (1H, dd, $^3J_{\text{HH}} = 7.1$ Hz, NH–CH, $^3J_{\text{HP}} = 18.9$ Hz, P=C–CH), 6.24–8.35 (22H, m, 3 C₆H₅ and C₁₄H₉NO₂), 10.41 (1H, d, $^3J_{\text{HH}} = 7.1$ Hz, CH–NH). ^{13}C NMR: 14.2 and 15.3 (2s, 2 OCH₂CH₃), 42.6 (d, $^1J_{\text{PC}} = 127.5$ Hz, P=C), 55.8 (d, $^2J_{\text{PC}} = 13.4$ Hz, P=C–CH), 58.7 and 61.4 (2s, 2 OCH₂CH₃), 113.2, 113.5, 115.3, 117.1, 120.1 and 123.5 (6 C, C₁₄H₉NO₂), 126.6 (d, $^1J_{\text{CP}} = 91.6$ Hz, C_{ipso} of 3 C₆H₅), 128.6 (d, $^3J_{\text{PC}} = 11.1$ Hz, C_{meta} of 2 C₆H₅), 132.0 (C_{para} of 3 C₆H₅), 132.5, 133.0 and 133.2 (3 C, C₁₄H₉NO₂), 133.7 (d, $^2J_{\text{PC}} = 9.9$ Hz, C_{ortho} of 3 C₆H₅), 149.7, 150.2 and 151.3 (3 C, C₁₄H₉NO₂), 165.0 (d, $^3J_{\text{PC}} = 12.6$ Hz, C=O_{ester}), 173.0 (d, $^2J_{\text{PC}} = 14.6$ Hz, P–C=C), 183.8 and 185.1 (2 C=O, C₁₄H₉NO₂). ^{31}P NMR: 22.4 (Ph₃P⁺–C).

Di-tert-butyl-2-(*N*-1-aminoanthraquinon-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3c). Red powder (0.53 g), yield 92%, mp 162–165°C. IR (KBr) (λ_{max} , cm^{–1}): 1598, 1631 (C=O), 1730 (C=O_{ester}), 3425 (N–H). MS (m/z , %): 711 (M⁺, 1), 684 (25), 402 (17), 277 (100), 262 (7), 223 (15), 183 (24), 77 (18), 57 (47). Anal. Calc. for C₄₄H₄₂NO₆P (711.78): C, 74.26; H, 5.91; N, 1.97%; Found: C, 74.35; H, 6.02; N, 1.89%.

Major isomer (E)-3c (63%): ^1H NMR: 0.99 and 1.48 (18H, 2s, 2 CMe₃), 5.08 (1H, dd, $^3J_{\text{HH}} = 5.5$ Hz, $^3J_{\text{HP}} = 24.8$ Hz, P=C–CH), 6.92–8.31 (22H, m, 3 C₆H₅ and C₁₄H₉NO₂), 10.02 (1H, d, $^3J_{\text{HH}} = 5.5$ Hz, CH–NH). ^{13}C NMR: 28.0 and 28.4 (2s, 2 CMe₃), 42.0 (d, $^1J_{\text{PC}} = 125.0$ Hz, P=C), 56.2 (d, $^2J_{\text{PC}} = 13.5$ Hz, P=C–CH), 78.0 and 81.7 (2s, 2 CMe₃), 113.0, 113.6, 115.1, 117.2, 120.4 and 123.2 (6C, C₁₄H₉NO₂), 127.3 (d, $^1J_{\text{PC}} = 90.6$ Hz, C_{ipso} of 3 C₆H₅), 128.5 (d, $^3J_{\text{PC}} = 10.2$ Hz, C_{meta} of 2 C₆H₅), 131.9 (C_{para} of 3 C₆H₅), 133.1, 133.2 and 133.3 (3C, C₁₄H₉NO₂), 133.9 (C_{ortho} of 3 C₆H₅), 149.8, 150.2 and 151.2 (3C, C₁₄H₉NO₂), 169.2 (d, $^2J_{\text{PC}} = 12.3$ Hz, C=O_{ester}), 171.9 (d, $^2J_{\text{PC}} = 14.0$ Hz, P–C=C), 184.3 and 185.2 (2C, C₁₄H₉NO₂). ^{31}P NMR: 19.9 (Ph₃P⁺–C).

Minor isomer (Z)-3c (37%): ^1H NMR: 1.55 and 1.57 (18H, 2s, 2 CMe_3), 4.20 (1H, dd, $^3J_{\text{HH}} = 5.3$ Hz, $^3J_{\text{HP}} = 24.5$ Hz, $\text{P}=\text{C}-\text{CH}$), 6.97–8.31 (22H, m, 3 C_6H_5 and $\text{C}_{14}\text{H}_9\text{NO}_2$), 10.54 (1H, d, $^3J_{\text{HH}} = 5.5$ Hz, $\text{CH}-\text{NH}$). ^{13}C NMR: 28.8 and 29.3 (2s, 2 CMe_3), 43.3 (d, $^1J_{\text{PC}} = 124.2$ Hz, $\text{P}=\text{C}$), 55.3 (d, $^2J_{\text{PC}} = 12.7$ Hz, $\text{P}=\text{C}-\text{CH}$), 80.7 and 81.1 (2s, 2 CMe_3), 114.8, 117.2, 118.0, 119.6, 120.4 and 124.7 (6C, $\text{C}_{14}\text{H}_9\text{NO}_2$), 126.4 (d, $^1J_{\text{PC}} = 92.3$ Hz, C_{ipso} of 3 C_6H_5), 128.2 (d, $^3J_{\text{PC}} = 9.8$ Hz, C_{meta} of 2 C_6H_5), 130.2 (C_{para} of 3 C_6H_5), 132.4, 133.6 and 132.9 (3C, $\text{C}_{14}\text{H}_9\text{NO}_2$), 133.9 (C_{ortho} of 3 C_6H_5), 149.9, 151.3 and 151.0 (3C, $\text{C}_{14}\text{H}_9\text{NO}_2$), 170.4 (d, $^2J_{\text{PC}} = 11.6$ Hz, $\text{C}=\text{O}_{\text{ester}}$), 171.7 (d, $^2J_{\text{PC}} = 13.7$ Hz, $\text{P}-\text{C}=\text{C}$), 183.5 and 183.8 (2C, $\text{C}_{14}\text{H}_9\text{NO}_2$). ^{31}P NMR: 22.4 ($\text{Ph}_3\text{P}^+-\text{C}$).

Dimethyl-2-(1,5-diphenylcarbazone-1-yl)-3-(triphenylphosphoranylidene) butanedioate (3d). Yellow powder (0.60 g), yield 94%, mp 115–118°C. IR (KBr) (λ_{max} , cm^{-1}): 1588 ($\text{N}=\text{N}$), 1636, 1735 ($\text{C}=\text{O}_{\text{ester}}$), 3430 ($\text{N}-\text{H}$). MS (m/z , %): 646 (M^++2 , 54), 277 (58), 92 (33), 77 (100), 57 (33). Anal. Calc. for $\text{C}_{37}\text{H}_{33}\text{N}_4\text{O}_5\text{P}$ (644.66): C, 68.94; H, 5.12; N, 8.70%; Found: C, 69.05; H, 5.18; N, 8.68%.

Major isomer (Z)-3d (59%): ^1H NMR: 3.07 and 3.82 (6H, 2s, 2 OCH_3), 5.13 (1H, d, $^3J_{\text{HP}} = 18.5$ Hz, $\text{P}=\text{C}-\text{CH}$), 1.30 (1H, br, NH), 6.86–7.91 (25H, m, 5 C_6H_5). ^{13}C NMR: 40.7 (d, $^1J_{\text{PC}} = 126.2$ Hz, $\text{P}=\text{C}$), 49.3 and 52.5 (2 OCH_3), 60.6 (d, $^2J_{\text{PC}} = 17.6$ Hz, $\text{P}=\text{C}-\text{CH}$), 113.3, 113.6, 114.2, 117.8, 120.5, 123.1 and 128.7 (7C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 126.1 (d, $^1J_{\text{PC}} = 92.1$ Hz, C_{ipso}), 128.7 (d, $^3J_{\text{PC}} = 12.7$ Hz, C_{meta}), 132.1 (d, $^4J_{\text{PC}} = 3.2$ Hz C_{para}), 133.4 (d, $^2J_{\text{PC}} = 9.9$ Hz, C_{ortho}), 146.1, 149.0, 149.9, 152.2 and 160.4 (5C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 167.0 (1C, $\text{O}=\text{C}-\text{N}$), 171.4 (d, $^3J_{\text{PC}} = 12.9$ Hz, $\text{C}=\text{O}_{\text{ester}}$), 173.38 (d, $^2J_{\text{PC}} = 11.32$ Hz, $\text{P}-\text{C}=\text{C}$). ^{31}P NMR: 23.8 ($\text{Ph}_3\text{P}^+-\text{C}$).

Minor isomer (E)-3d (41%): ^1H NMR: 3.16 and 3.84 (6H, 2s, 2 OCH_3), 5.02 (1H, d, $^3J_{\text{HP}} = 16.8$ Hz, $\text{P}=\text{C}-\text{CH}$), 1.30 (1H, br, NH), 6.80–7.55 (25H, m, 5 C_6H_5). ^{13}C NMR: 40.3 (d, $^1J_{\text{PC}} = 126.6$ Hz, $\text{P}=\text{C}$), 52.5 and 52.9 (2 OCH_3), 61.5 (d, $^2J_{\text{PC}} = 17.1$ Hz, $\text{P}=\text{C}-\text{CH}$), 113.2, 113.4, 114.0, 118.2, 120.1, 124.1 and 129.1 (7C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 126.0 (d, $^1J_{\text{PC}} = 92.1$ Hz, C_{ipso}), 128.6 (d, $^3J_{\text{PC}} = 12.1$ Hz, C_{meta}), 132.0 (d, $^4J_{\text{PC}} = 3.2$ Hz, C_{para}), 133.5 (d, $^2J_{\text{PC}} = 9.8$ Hz, C_{ortho}), 147.3, 148.9, 149.4, 151.5 and 160.3 (5C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 165.4 (1C, $\text{O}=\text{C}-\text{N}$), 171.0 (d, $^3J_{\text{PC}} = 12.7$ Hz, $\text{C}=\text{O}_{\text{ester}}$), 172.3 (d, $^2J_{\text{PC}} = 10.3$ Hz, $\text{P}-\text{C}=\text{C}$). ^{31}P NMR: 23.9 ($\text{Ph}_3\text{P}^+-\text{C}$).

Diethyl-2-(1,5-diphenylcarbazone-1-yl)-3-(triphenylphosphoranylidene) butanedioate (3e). Yellow crystal (0.60 g), yield 90%, mp 177–180°C. IR (KBr) (λ_{max} , cm^{-1}): 1620 ($\text{N}=\text{N}$), 1720, 1732 ($\text{C}=\text{O}_{\text{ester}}$), 3433 ($\text{N}-\text{H}$). MS (m/z , %): 672 (M^++2 , 13), 446 (10), 277 (100), 199 (24), 183 (22), 152 (14), 134 (10), 92 (25), 77 (59). Anal. Calc. for $\text{C}_{39}\text{H}_{37}\text{N}_4\text{O}_5\text{P}$ (672.71): C, 69.64; H, 5.51; N, 8.33%; Found: C, 69.71; H, 5.48; N, 8.38%.

Major isomer (Z)-3e (67%): ^1H NMR: 0.43 and 1.39 (6H, 2t, $^3J_{\text{HH}} = 7.1$ Hz 2 OCH_2CH_3), 1.70 (1H, br, NH), 4.21–4.44 (4H, m, 2 ABX_3 system, 2 OCH_2CH_3), 5.12 (1H, d, $^3J_{\text{HP}} = 18.4$ Hz, $\text{P}=\text{C}-\text{CH}$), 6.84–7.80 (25H, m, 5 C_6H_5). ^{13}C NMR: 14.0 and 14.3 (2s, 2 OCH_2CH_3), 40.0 (d, $^1J_{\text{PC}} = 126.8$ Hz, $\text{P}=\text{C}$), 58.0 and 61.8 (2 OCH_2CH_3), 61.7 (d, $^2J_{\text{PC}} = 17.8$ Hz, $\text{P}=\text{C}-\text{CH}$), 113.0, 113.3, 113.8, 117.9, 122.5, 123.1 and 124.1 (7C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 126.2 (d, $^1J_{\text{PC}} = 92.1$ Hz, C_{ipso}), 128.7 (d, $^3J_{\text{PC}} = 11.9$ Hz, C_{meta}), 132.9 (d, $^4J_{\text{PC}} = 2.6$ Hz, C_{para}), 133.6 (d, $^2J_{\text{PC}} = 10.0$ Hz, C_{ortho}), 146.0, 148.9, 149.9, 152.2 and 160.9 (5C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 167.3 (1C, $\text{O}=\text{C}-\text{N}$), 170.7 (d, $^3J_{\text{PC}} = 12.8$ Hz, $\text{C}=\text{O}_{\text{ester}}$), 172.8 (d, $^2J_{\text{PC}} = 11.6$ Hz, $\text{P}-\text{C}=\text{C}$). ^{31}P NMR: 23.8 ($\text{Ph}_3\text{P}^+-\text{C}$).

Minor isomer (E)-3e (33%): ^1H NMR: 1.26 and 1.29 (6H, 2t, $^3J_{\text{HH}} = 7.0$ Hz, 2 OCH_2CH_3), 1.70 (1H, br, NH), 4.15–4.44 (4H, m, 2 ABX_3 system, 2 OCH_2CH_3), 5.18

(1H, d, $^3J_{\text{HP}} = 18.6$ Hz, $\text{P}=\text{C}-\text{CH}$), 6.84–7.80 (25H, m, 5 C_6H_5). ^{13}C NMR: 13.8 and 14.1 (2 OCH_2CH_3), 40.4 (d, $^1J_{\text{PC}} = 126.0$ Hz, $\text{P}=\text{C}$), 58.4 and 61.3 (2 OCH_2CH_3), 62.2 (d, $^2J_{\text{PC}} = 17.7$ Hz, $\text{P}=\text{C}-\text{CH}$), 113.2, 113.6, 114.3, 118.1, 121.4, 123.1 and 125.4 (7C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 126.3 (d, $^1J_{\text{PC}} = 92.1$ Hz, C_{ipso}), 128.6 (d, $^3J_{\text{PC}} = 11.8$ Hz, C_{meta}), 131.9 (d, $^4J_{\text{PC}} = 2.6$ Hz C_{para}), 133.5 (d, $^2J_{\text{PC}} = 10.3$ Hz, C_{ortho}), 147.2, 149.1, 150.1, 151.4 and 160.5 (5C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 165.0 (1C, $\text{O}=\text{C}-\text{N}$), 170.7 (d, $^3J_{\text{PC}} = 12.7$ Hz, $\text{C}=\text{O}_{\text{ester}}$), 171.7 (d, $^2J_{\text{PC}} = 10.4$ Hz, $\text{P}-\text{C}=\text{C}$). ^{31}P NMR: 23.9 ($\text{Ph}_3\text{P}^+-\text{C}$).

Di-tert-buthyl-2-(1,5-diphenylcarbazone-1-yl)-3-(triphenylphosphoranylidene)butanedioate (3f). Pale white powder (0.70 g), yield 96%, m.p. 172–175°C. IR (KBr) (λ_{max} , cm^{-1}): 1598 ($\text{N}=\text{N}$), 1688, 1728 ($\text{C}=\text{O}_{\text{ester}}$), 3427 ($\text{N}-\text{H}$). MS (m/z , %): 728 (M^+ , 4), 489 (21), 377 (40), 277 (40), 262 (98), 183 (100), 152 (22), 108 (53), 93 (95), 57 (58). Anal. Calc. for $\text{C}_{43}\text{H}_{45}\text{N}_4\text{O}_5\text{P}$ (728.81): C, 70.88; H, 6.18; N, 7.69%; Found: C, 70.91; H, 6.09; N, 7.75%.

Major isomer (Z)-3f (79%): ^1H NMR: 0.88 and 1.61 (18H, 2s, 2 CMe_3), 5.00 (1H, d, $^3J_{\text{HP}} = 18.3$ Hz, $\text{P}=\text{C}-\text{CH}$), 1.28 (1H, br, NH), 6.80–7.92 (25H, m, 5 C_6H_5). ^{13}C NMR: 28.3 and 28.4 (2 CMe_3), 39.9 (d, $^1J_{\text{PC}} = 126.3$ Hz, $\text{P}=\text{C}$), 61.4 (d, $^2J_{\text{PC}} = 17.8$ Hz, $\text{P}=\text{C}-\text{CH}$), 77.5 and 81.2 (2 OCMe_3), 113.2, 113.4, 119.9, 120.0, 121.2 and 123.2 (6C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 126.7 (d, $^1J_{\text{PC}} = 92.0$ Hz, C_{ipso}), 128.5 (d, $^3J_{\text{PC}} = 12.0$ Hz, C_{meta}), 132.0 (C_{para}), 133.7 (d, $^2J_{\text{PC}} = 9.5$ Hz, C_{ortho}), 147.2, 149.0, 149.2, 150.0, 159.6 and 160.7 (6C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 164.4 (1C, $\text{O}=\text{C}-\text{N}$), 170.5 (d, $^3J_{\text{PC}} = 12.1$ Hz, $\text{C}=\text{O}_{\text{ester}}$), 172.0 (d, $^2J_{\text{PC}} = 11.9$ Hz, $\text{P}-\text{C}=\text{C}$). ^{31}P NMR: 23.5 ($\text{Ph}_3\text{P}^+-\text{C}$).

Minor isomer (E)-3f (23%): ^1H NMR: 1.43 and 1.55 (18H, 2s, 2 CMe_3), 4.87 (1H, d, $^3J_{\text{HP}} = 18.9$ Hz, $\text{P}=\text{C}-\text{CH}$), 1.22 (1H, br, NH), 6.80–7.92 (25H, m, 5 C_6H_5). ^{13}C NMR: 28.0 and 28.1 (2 CMe_3), 39.6 (d, $^1J_{\text{PC}} = 126.9$ Hz, $\text{P}=\text{C}$), 61.4 (d, $^2J_{\text{PC}} = 17.8$ Hz, $\text{P}=\text{C}-\text{CH}$), 81.7 and 82.0 (2 OCMe_3), 113.3, 113.8, 120.3, 120.6, 123.7 and 124.1 (6C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 126.7 (d, $^1J_{\text{PC}} = 92.0$ Hz, C_{ipso}), 128.4 (d, $^3J_{\text{PC}} = 12.3$ Hz, C_{meta}), 132.0 (C_{para}), 133.6 (d, $^2J_{\text{PC}} = 9.5$ Hz, C_{ortho}), 148.4, 149.0, 151.4, 152.1, 159.6 and 161.1 (6C, $(\text{C}_6\text{H}_5)_2\text{N}_4\text{HCO}$), 167.4 (1C, $\text{O}=\text{C}-\text{N}$), 170.5 (d, $^3J_{\text{PC}} = 12.1$ Hz, $\text{C}=\text{O}_{\text{ester}}$), 170.6 (d, $^2J_{\text{PC}} = 10.5$ Hz, $\text{P}-\text{C}=\text{C}$). ^{31}P NMR: 23.6 ($\text{Ph}_3\text{P}^+-\text{C}$).

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