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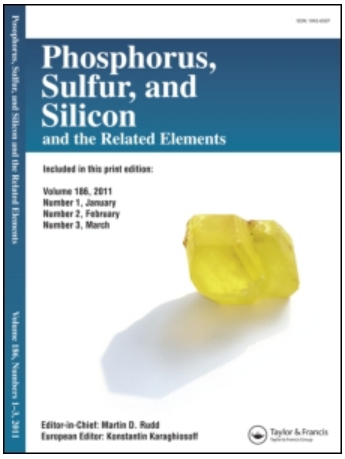

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A Simple Synthesis of Stable Heterocyclic Phosphorus Ylides Derived from NH-Acids

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A SIMPLE SYNTHESIS OF STABLE HETEROCYCLIC PHOSPHORUS YLIDES DERIVED FROM NH-ACIDS

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(Received August 21, 2001)

Crystalline phosphorus ylides are obtained in excellent yields from the addition reaction between triphenylphosphine, dimethyl acetylenedicarboxylate and strong NH-acids, such as 2-acetylpyrrole, indole, ethyl 3-indolylglyoxalate and N*-benzyl-2-pyrrolylglyoxamate. Dynamic NMR effects are observed in the* ^{1}*H NMR spectra of stabilized ylides obtained from 2-acetylpyrrole and indole (*$\Delta G^{\neq} = 67.1$ *and 68.8 kJmol*$^{-1}$ *respectively) and are attributed to restricted rotation around the carbon-carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group.*

Keywords: Acetylenic ester; NH-acids; stable phosphorus ylides; triphenylphosphine

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INTRODUCTION

Phosphorus ylides are reactive intermediates, which take part in many valuable reactions in organic synthesis.[1–12] Several methods have been developed for the preparation of phosphorus ylides. 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.[1–3] Phosphonium salts are also prepared by Michael addition of phosphorus nucleophiles to activated olefins among other methods.[1] We report here an efficient synthetic route to phosphorus ylides using triphenylphosphine, dimethyl acetylenedicarboxylate (DMAD) and heterocyclic NH-acids, such as 2-acetylpyrrole, indole and ethyl 3-indolylglyoxalate. Thus, reaction of NH-acids **1** with DMAD in the presence of triphenylphosphine leads to the corresponding stable heterocyclic phosphorus ylides **2** in exellent yields (Scheme 1).

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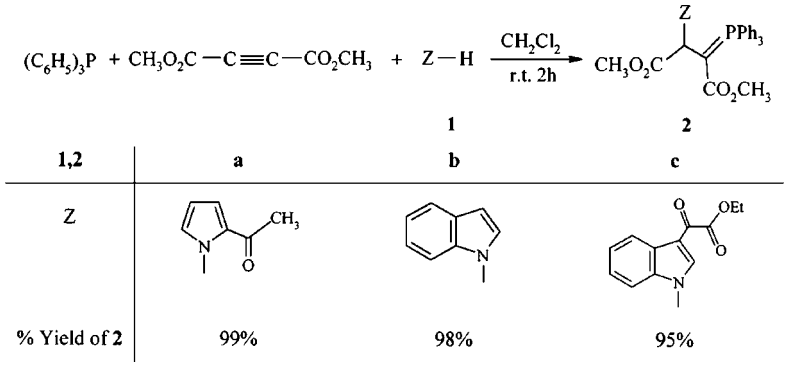

SCHEME 1

RESULTS AND DISCUSSION

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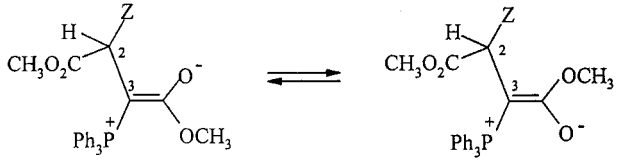
The reaction of heterocyclic NH-acids **1** with dimethyl acetylenedicarboxylate in the presence of triphenylphosphine proceeded spontaneously at room temperature in dichloromethane, and was finished within 1–2 h. ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of phosphorane **2**. Any product other than **2** could not be detected by NMR spectroscopy.

The structures of compounds **2a–c** were deduced from their elemental analyses and their high-field ^{1}H, ^{13}C, and ^{31}P NMR and IR spectral data. The nature of these compounds as 1:1:1 adducts were apparent from their mass spectra which displayed molecular ion peaks at $m/z =$ 513, 521, and 621 respectively. Initial fragmentations involve loss from or complete loss of the side chains and scission of the heterocyclic ring system.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **2a–c** are consistent with the presence of two isomers. 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 **2a–c** are shown in Table I. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation about the partial double bond in **2**-(*E*) and **2**-(*Z*) geometrical isomers (see Figure 1) is slow on the NMR timescale at ambient temperature.

The most noteworthy feature of the ^{1}H NMR spectrum of **2a** in $CDCl_3$ at room temperature (25°C) is the methoxy region which exhibits two sharp singlets ($\delta = 3.72$ and 3.73 ppm) for the CO_2CH_3 groups of (*E*)-**2a** and (*Z*)-**2a** and two fairly broad singlets ($\delta = 3.21$ and 3.59) for the methoxy groups. Near 5°C the broad lines become sharper. The ^{1}H NMR spectrum of **2a** was examined in 1,2-dichlorobenzene. At 5°C

TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-2, CO_2CH_3, $COCH_3$, C-2, C-3, and P in the Major (M) and Minor (m) Geometrical Isomers of Compounds **2a–c**

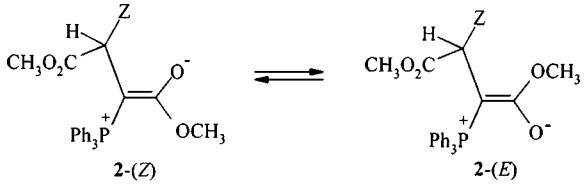


2-(*Z*), Major **2**-(*E*), Minor

Compound	Isomer (%)	^{1}H NMR spectroscopic data			^{13}C NMR spectroscopic data		^{31}P
		H-2 ($^{3}J_{PH}$)	OCH_3	CO_2CH_3	C-2 ($^{2}J_{PC}$)	C-3 ($^{1}J_{PC}$)	
2a	M(55)	5.75 (19.2)	3.21	3.73	60.59 (12.5)	43.87 (134.9)	24.45
	m(45)	5.81 (17.8)	3.59	3.72	60.73 (12.9)	43.52 (126.9)	25.35
2b	M(53)	4.95 (16.1)	3.25	3.69	58.14 (15.7)	43.76 (126.7)	24.75
	m(47)	4.97 (18.1)	3.67	3.68	57.74 (15.7)	44.12 (135.1)	24.07
2c	M(60)	4.90 (15.6)	3.25	3.70	59.21 (16.0)	41.01 (127.7)	24.69
	m(40)	4.92 (17.0)	3.67	3.69	58.65 (15.5)	42.81 (136.2)	24.14

the spectrum is similar to that in $CDCl_3$. Increasing the temperature results in coalescence of the methoxy resonances ($T_c = 48 \pm 1°C$). At 90°C, a fairly broad singlet was observed, while the CO_2CH_3 protons appear as a sharp single resonance.

Although an extensive line-shape analysis in relation to the dynamic ^{1}H NMR effect observed for **2a** was not undertaken, the variable temperature spectra allowed to calculate the free energy barrier (if not the enthalpy and entropy of activation) for the dynamic NMR process in **2a**. From coalescence of the methoxy proton resonances and using the expression, $k = \pi\Delta\nu/\sqrt{2}$, we calculate that the first-order rate constant (k) for the dynamic NMR effect in **2a** is 77 s^{-1} at 321 K (see Table II). Application of the absolute rate theory with a transmission coefficient of 1 gives a free-energy of activation ($\Delta G^{\neq}$) of 67.1 ± 2 $kJmol^{-1}$, where all known sources of errors are estimated and included.[13] The experimental data available are not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, even though the errors in $\Delta G^{\neq}$ are not large.[14]



2-(*Z*) **2**-(*E*)

FIGURE 1.

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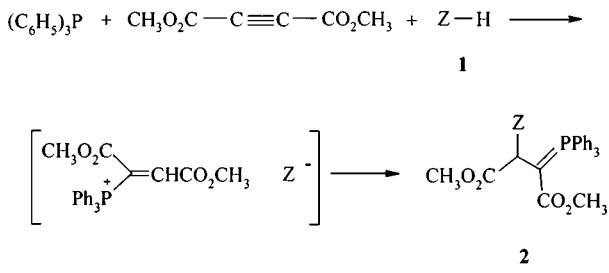
TABLE II Selected Proton Chemical Shifts (at 90 MHz, in ppm, Me_4Si) and Activation Parameters ($kJmol^{-1}$) for **2a** and **2b** in 1,2-Dichlorobenzene

Compound	Temp (°C)	Resonance (OCH_3)		$\Delta\nu$ (Hz)	k (s^{-1})	T_c (K)	$\Delta G^{\neq}$
2a	5	3.21	3.59	35	77	321	67.1 ± 2
	90	3.42					
2b	5	3.25	3.67	38	85	330	68.8 ± 2
	90	3.46					

Similar dynamic ^1H NMR effect was observed for compound **2b**. From coalescence of the methoxy proton resonances, the first-order rate constant for the dynamic NMR in **2b** is 85 s^{-1} at 330 K. The calculated free-energy of activation for the dynamic process in **2b** is 68.8 ± 2 $kJmol^{-1}$ (see Table II).

Dynamic NMR effects observed in the ^1H NMR spectra of compounds **2a** and **2b** are attributed to restricted rotation around the carbon-carbon partial double bond resulting from conjugation of the phosphorus ylide carbon atom with the adjacent carbonyl group.

On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[1–12] it is reasonable to assume that phosphorus ylide **2** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the NH-acid **1**. Then the positively charged ion is attacked by the nitrogen atom of the conjugate base of the NH-acid to form phosphoranes **2** (Scheme 2).



SCHEME 2

N-benzyl-2-pyrrolylglyoxamate **1d** possesses two acidic N-H protons. Thus, the reaction of **1d** with two equivalents of DMAD in the presence of two equivalents of triphenylphosphine leads to the formation of bis-ylide **2d** in nearly quantitative yield (see Scheme 3). Compound **2d** possesses two chirality centers, thus it can exist in two diastereoisomeric forms, namely *S*,S and *R*,S. These diastereoisomers are formed in nearly 1:1 ratio and are separated by fractional crystallization from 1:1

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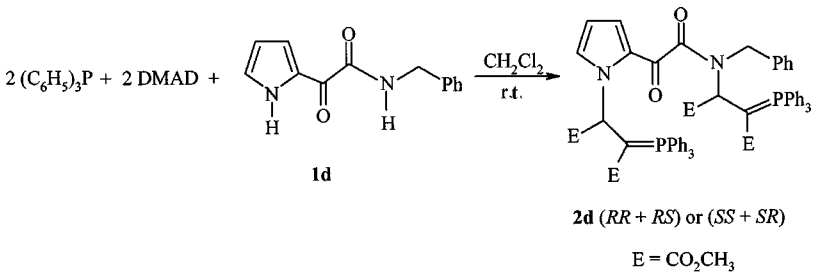
hexane-ethyl acetate solvent mixture. Both diastereomers are colorless crystalline compounds. The methoxy region of the ^{1}H NMR spectrum of the compound with lower melting point (152–155°C), which we named isomer **A**, exhibits sixteen sharp singlets as a result of restricted rotation around the partial carbon-carbon double bonds of the two ylidic moieties. In fact, isomer **A** consists of four rotamers, namely *E*,*Z*; *E*,*E*; *Z*,*E*; and *Z*,*Z*. The ^{1}H NMR spectrum of the higher melting (202–205°C) isomer **B** also exhibits 16 sharp singlets in the methoxy region in agreement with the presence of 4 rotational isomers. The ^{13}C NMR spectrum of diastereoisomers **A** or **B** is consistent with the presence of 4 rotamers. Partial assignments of the ^{1}H, ^{13}C, and ^{31}P resonances of the two diastereoisomers **A** and **B** are given in the Experimental section.



SCHEME 3

Functionalized heterocyclic phosphorus ylides **2a–d** may be considered as potentially useful synthetic intermediates.[1–3] The procedure described here may be an acceptable method for the preparation of phosphoranes with variable functionalities. The one-pot nature of the present procedure makes it an interesting alternative to multistep approaches.[1–10]

EXPERIMENTAL

Indole, 2-acetylpyrrole, DMAD and triphenylphosphine were obtained from Fluka (Buchs, Switzerland) and were used without further purification. Ethyl 3-indolylglyoxalate and *N*-benzyl-2-pyrrolylglyoxamate were prepared by known methods.[15,16] Melting points were measured on an Electrothermal 9100 apparatus. Elemental analyses for C, H, and N were performed using a Heraeus CHN—O-Rapid analyzer. Mass spectra were recorded on a FINNIGAN-MATT 8430 mass spectrometer operating at an ionization potential of 70 eV. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured ($CDCl_3$ solution) with a Brucker DRX-500 AVANCE

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spectrometer at 500.1, 125.8, and 202.5 MHz respectively. Dynamic NMR studies were carried out using a JEOL-EX 90 Fourier transform spectrometer at 89.45 MHz. IR spectra were recorded on a Shimadzu IR-460 spectrometer.

Preparation of Dimethyl 2-(2-acetyl-1*H*-pyrrol-1-yl)-3-(triphenylphosphoranylidene)butanedioate 2a: General Procedure

To a magnetically stirred solution of 0.52 g triphenylphosphine (2 mmol) and 0.22 g 2-acetylpyrrole (2 mmol) in 4 mL of dichloromethane was added dropwise a mixture of 0.28 g DMAD (2 mmol) in 2 mL of dichloromethane at −5°C for 10 min. The reaction mixture was then allowed to warm to room temperature and stirred for 3 h. The solvent was removed under reduced pressure and the residual solid recrystallized from hexane-ethyl acetate to give colorless crystals; m.p. 183–185°C; yield 1.02 g, 99%; IR (KBr) (υ_{max}/cm^{-1}): 1721 and 1616 (C=O); MS, *m/z* (%): 513 (M^+, 4), 408 (8), 405 (25), 262 (100), 183 (50), 108 (34), 51 (22); Anal. Calcd. for $C_{30}H_{28}NO_5P$ (513.53): C, 70.17; H, 5.50; N, 2.73. Found: C, 70.5; H, 5.4; N, 2.7%.

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Major isomer, **2a**-(Z) (55%), ^{1}H NMR: δ 2.16 (3 H, s, CH_3), 3.21 and 3.73 (6 H, 2 s, 2 OCH_3), 5.75 (1 H, d, $^3J_{PH}$ 19.2 Hz, P–C–CH), 6.18 (1 H, br t, N–CH=C*H*), 6.88 (1 H, br t, N–C=CH), 7.3–7.6 (15 H, m, 3 C_6H_5), 7.66 (1 H, br t, N–C*H*=CH). ^{13}C NMR: δ 26.93 (CH_3), 43.87 (d, $^1J_{PC}$ 134.9 Hz, P=C), 49.29 and 52.34 (2 OCH_3), 60.59 (d, $^2J_{PC}$ 12.5 Hz, P–C–*C*H), 107.75 (pyrrole C^4H), 119.78 (pyrrole C^3H), 125.49 (d, $^1J_{PC}$ 92.2 Hz, C^{ipso}), 128.33 (pyrrole C^5H), 128.76 (d, $^3J_{PC}$ 11.9 Hz, C^m), 130.13 (pyrrole C^2), 132.12 (C^p), 133.39 (d, $^2J_{PC}$ 9.4 Hz, C^o), 170.57 and 172.62 (2 d, $^2J_{PC}$ 13.7 Hz and $^3J_{PC}$ 18.5 Hz, 2 C=O ester), 187.35 (pyrrole-C=O). ^{31}P NMR: δ 24.45 (Ph_3P^+–C).

Minor isomer, **2a**-(*E*) (45%), ^{1}H NMR: δ 2.12 (3 H, s, CH_3), 3.59 and 3.72 (6 H, 2 s, 2 OCH_3), 5.81 (1 H, d, $^3J_{PH}$ 17.8 Hz, P–C–CH), 6.16 (1 H, br t, N–CH=C*H*), 6.82 (1 H, br t, N–C=CH), 7.3–7.6 (15 H, m, 3 C_6H_5), 7.72 (1 H, br t, N–C*H*=CH). ^{13}C NMR: δ 26.89 (CH_3), 43.52 (d, $^1J_{PC}$ 126.9 Hz, P=C), 50.32 and 52.52 (2 OCH_3), 60.73 (d, $^2J_{PC}$ 12.9 Hz, P–C–*C*H), 107.74 (pyrrole C^4H), 119.55 (pyrrole C^3H), 126.12 (d, $^1J_{PC}$ 91.7 Hz, C^{ipso}), 128.69 (d, $^3J_{PC}$ 11.8 Hz, C^m), 129.06 (pyrrole C^5H), 129.87 (pyrrole C^2), 132.13 (C^p), 133.32 (d, $^2J_{PC}$ 9.1 Hz, C^o), 169.86 and 172.57 (2 d, $^2J_{PC}$ 13.6 Hz and $^3J_{PC}$ 13.2 Hz, 2 C=O ester), 187.12 (pyrrole-C=O). ^{31}P NMR: δ 25.35 (Ph_3P^+–C).

*Dimethyl 2-(1*H*-indol-1-yl)-3-(triphenylphosphoranylidene)butanedioate (**2b**)*: colorless crystals; m.p. 193–195°C; yield 1.04 g, 98%; IR (KBr) (υ_{max}/cm^{-1}): 1749 and 1613 (C=O); MS, *m/z* (%): 521 (M^+, 2),

462 (10), 405 (70), 262 (100), 183 (68), 108 (50), 51 (20); Anal. Calcd. for $C_{32}H_{28}NO_4P$ (521.55): C, 73.69; H, 5.41; N, 2.69. Found: C, 73.6; H, 5.4; N, 2.7%.

Major isomer, **2b**-(*Z*) (53%), ^{1}H NMR: δ 3.25 and 3.69 (6 H, 2 s, 2 OCH_3), 4.95 (1 H, d, $^3J_{PH}$ 16.1 Hz, P—C—CH), 6.17 (1 H, d, *J* 8.2 Hz, CH), 6.53 (1 H, d, *J* 9.8 Hz, CH), 6.85 (1 H, dd, *J* 7.4 Hz and *J* 8.2 Hz, CH), 6.96 (1 H, dd, *J* 7.5 Hz and *J* 6.7 Hz, CH), 7.35–7.65 (16 H, m, 3 C_6H_5 and CH), 7.83 (1 H, d, *J* 3 Hz, CH). ^{13}C NMR: δ 43.76 (d, $^1J_{PC}$ 126.7 Hz, P=C), 49.43 and 52.66 (2 OCH_3), 58.14 (d, $^2J_{PC}$ 15.7 Hz, P—C—*C*H), 101.29 (CH), 108.54 (C), 118.87 and 120.53 (2 CH), 126.51 (d, $^1J_{PC}$ 91.9 Hz, C^{ipso}), 128.04 and 128.45 (2 CH), 128.98 (d, $^3J_{PC}$ 12.2 Hz, C^m), 132.28 (d, $^4J_{PC}$ 2.5 Hz, C^p), 133.59 (d, $^2J_{PC}$ 9.4 Hz, C^o), 135.99 (C—N), 170.75 and 173.10 (2 d, $^2J_{PC}$ 12.8 Hz and $^3J_{PC}$ 13.7 Hz, 2 C=O ester). ^{31}P NMR: δ 24.75 (Ph_3P^+—C).

Minor isomer, **2b**-(Z) (47%), ^{1}H NMR: δ 3.67 and 3.68 (6 H, 2 s, 2 OCH_3), 4.97 (1 H, d, $^3J_{PH}$ 18.1 Hz, P—C—CH), 6.22 (1 H, d, *J* 8.2 Hz, CH), 6.54 (1 H, d, *J* 9.8 Hz, CH), 6.88 (1 H, dd, *J* 8.7 Hz and *J* 7.8 Hz, CH), 6.99 (1 H, dd, *J* 6.7 Hz and *J* 7.4 Hz, CH), 7.35–7.65 (16 H, m, 3 C_6H_5 and CH), 7.75 (1 H, d, *J* 3 Hz, CH). ^{13}C NMR: δ 44.12 (d, $^1J_{PC}$ 135.1 Hz, P=C), 50.46 and 52.52 (2 OCH_3), 57.74 (d, $^2J_{PC}$ 15.7 Hz, P—C—CH), 101.28 (CH), 108.66 (C), 119.07 and 120.65 (2 CH), 125.87 (d, $^1J_{PC}$ 92.3 Hz, C^{ipso}), 127.06 and 128.57 (2 CH), 129.01 (d, $^3J_{PC}$ 12.2 Hz, C^m), 132.26 (d, $^4J_{PC}$ 2.5 Hz, C^p), 133.66 (d, $^2J_{PC}$ 7.5 Hz, C^o), 136.16 (C—N), 170.59 and 172.88 (2 d, $^2J_{PC}$ 14.1 Hz and $^3J_{PC}$ 17.8 Hz, 2 C=O ester). ^{31}P NMR: δ 24.07 (Ph_3P^+—C).

*Dimethyl 2-[3-(2-ethoxy-2-oxoacetyl)-1*H*-indol-1-yl]-3-(triphenylphosphoranylidene) butanedioate (**2c**)*: Colorless crystals; m.p. 151–153°C; yield 1.2 g, 95%; IR (KBr) (υ_{max}/cm^{-1}): 1742 and 1627 (C=O); MS, *m/z* (%): 622 (M^+, 2), 549 (4), 405 (50), 262 (100), 228 (10), 183 (85), 144 (82), 108 (70), 51 (28); Anal. Calcd. for $C_{36}H_{32}NO_7P$ (621.63): C, 69.56; H, 5.89; N, 2.25. Found: C, 69.4; H, 5.3; N, 2.3%.

Major isomer, **2c**-(Z) (60%), ^{1}H NMR: δ1.45 (3 H, t, *J* 7 Hz, CH_3), 3.25 and 3.70 (6 H, 2 s, 2 OCH_3), 4.44 (2 H, q, *J* 7 Hz, OCH_2), 4.90 (1 H, d, $^3J_{PH}$ 15.6 Hz, P—C—CH), 6.29 (1 H, d, *J* 8 Hz, CH), 6.97 (1 H, t, *J* 7.4 Hz, CH), 7.16 (1 H, t, *J* 7.4 Hz, CH), 7.3–7.6 (15 H, m, 3 C_6H_5), 8.33 (1 H, d, *J* 7.5 Hz, CH), 8.93 (1 H, d, *J* 7.5 Hz, CH). ^{13}C NMR: δ 13.62 (CH_3), 41.01 (d, $^1J_{PC}$ 127.7 Hz, P=C), 49.11 and 52.45 (2 OCH_3), 59.21 (d, $^2J_{PC}$ 16 Hz, P—C—CH), 61.28 (OCH_2), 108.75 and 112.61 (2 C), 121.90, 122.43 and 122.85 (3 CH), 125.34 (d, $^1J_{PC}$ 92.2 Hz, C^{ipso}), 126.28 (CH), 128.60 (d, $^3J_{PC}$ 12.2 Hz, C^m), 131.98 (C^p), 132.95 (d, $^2J_{PC}$ 9.3 Hz, C^o), 136.35 (C—N), 162.75 ($CO_2C_2H_5$), 169.49 and 170.85 (2 d, $^2J_{PC}$ 12.2 Hz and $^3J_{PC}$ 12.2 Hz, 2 C=O ester), 178.05 (C=O). ^{31}P NMR: δ 24.69 (Ph_3P^+—C).

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Minor isomer, **2c**-(*E*) (40%), ^{1}H NMR: δ 1.44 (3 H, t, *J* 7 Hz, CH_3), 3.67 and 3.69 (6 H, 2 s, 2 OCH_3), 4.43 (2 H, q, *J* 7 Hz, OCH_2), 4.92 (1 H, d, $^3J_{PH}$ 17 Hz, P–C–CH), 6.28 (1 H, d, *J* 8 Hz, CH), 6.99 (1 H, t, *J* 7.5 Hz, CH), 7.17 (1 H, t, *J* 7.3 Hz, CH), 7.3–7.6 (15 H, m, 3 C_6H_5), 8.32 (1 H, d, *J* 7.5 Hz, CH), 8.94 (1 H, d, *J* 7.5 Hz, CH). ^{13}C NMR: δ 13.64 (CH_3), 42.81 (d, $^1J_{PC}$ 136.2 Hz, P=C), 50.00 and 52.32 (2 OCH_3), 58.65 (d, $^2J_{PC}$ 15.5 Hz, P–C–CH), 61.29 (OCH_2), 108.76 and 112.63 (2 C), 121.95, 122.53 and 122.96 (3 CH), 124.76 (d, $^1J_{PC}$ 93.2 Hz, C^{ipso}), 126.40 (CH), 128.62 (d, $^3J_{PC}$ 12.2 Hz, C^m), 131.95 (C^p), 132.95 (d, $^2J_{PC}$ 9.3 Hz, C^o), 136.45 (C–N), 162.61 ($CO_2C_2H_5$), 169.85 and 170.65 (2 d, $^2J_{PC}$ 14.1 Hz and $^3J_{PC}$ 16 Hz, 2 C=O ester), 177.66 (C=O). ^{31}P NMR: δ 24.14 (Ph_3 P^+–C).

*Dimethyl 2-[2-(2-{benzyl[3-methoxy-1-(methoxycarbonyl)-3-oxo-2-(triphenylphosphoranylidene)propyl]amino}-2-oxoacetyl)-1*H*-pyrrol-1-yl]-3-(triphenylphosphanylidene)butanedioate*, (**2d**, diastereoisomer **A**): Colorless crystals; yield 1.14 g, 55%; m.p. 152–155°C; IR (KBr) (υ_{max}/cm^{-1}): 1729 and 1621 (C=O); MS, *m/z* (%): 1037 (M^+, 1), 638 (8), 496 (40), 464 (25), 277 (56), 262 (50), 183 (100), 91 (78), 51 (30); Anal. Calcd. for $C_{61}H_{54}N_2O_{10}P_2$ (1037.06): C, 70.65; H, 5.25; N, 2.70%. Found: C, 70.3; H, 5.3; N, 2.6%. ^{1}H NMR: δ 3.02, 3.03, 3.17, 3.23, 3.33, 3.34, 3.35, 3.37, 3.45, 3.46, 3.53, 3.55, 3.60, 3.62, 3.75 and 3.82 (12 H, 16 s, 4 OCH_3), 4.2–4.8 (2 H, m, NCH_2), 4.98, 5.01, 5.20, 5.23, 5.62, 5.63, 5.75 and 5.76 (2 H, 8 d, $^3J_{PH}$ 16.8, 16.6, 21.0, 19.6, 19.0, 18.2, 19.1 and 17.3 Hz, 2 P–C–CH), 6.1–6.4 (1 H, m, N–CH=C*H*), 7.1–7.9 (37 H, m, 2 $P(C_6H_5)_3$, $NCH_2C_6H_5$, NC*H*=CH and N–C=CH). ^{13}C NMR: δ 40.89, 41.34, 42.42, 43.12 and 43.14 (5 d, $^1J_{PC}$ 123.3, 127.5, 126.6, 135.2 and 135.5 Hz, P=C), 48.91, 48.95, 49.25, 49.40, 49.80, 50.32, 52.07 and 52.26 (OCH_3), 56.95, 56.98, 57.07 and 57.10 (NCH_2), 61.52 and 61.84 (2 d, $^3J_{PC}$ 16.8 and 17.9 Hz, P–C–*C*H), 108.94, 108.97, 109.06 and 109.15 (pyrrole C^4H), 125.52, 125.95, 126.05 and 126.55 (4 d, $^1J_{PC}$ 92.7, 94.4, 92.1 and 91.7 Hz, C^{ipso}), 126.6–128.8 (pyrrole C^5, C^p of CH_2Ph, C^m, C^o of CH_2Ph and C^m of CH_2Ph), 131–132 (pyrrole C^2 and C^p), 132.9–133.2 (C^o), 168–172 (C=O), 180.25, 180.44, 180.71 and 180.93 (pyrrole-C=O). ^{31}P NMR: δ 24.36, 24.98, 25.19 and 25.98 (Ph_3P^+–C).

*Dimethyl 2-[2-(2-{benzyl[3-methoxy-1-(methoxycarbonyl)-3-oxo-2-(triphenylphosphoranylidene)propyl]amino}-2-oxoacetyl)-1*H*-pyrrol-1-yl]-3-(triphenylphosphanylidene)butanedioate*, (**2d**, diastereoisomer **B**): Colorless crystals; yield 0.9 g, 45%; m.p. 202–203°C; IR (KBr) (υ_{max}/cm^{-1}): 1726 and 1624 (C=O); MS, *m/z* (%): 1037 (M^+, 2), 638 (15), 496 (45), 464 (15), 277 (44), 262 (55), 183 (100), 91 (70), 51 (35); Anal. Calcd. for $C_{61}H_{54}N_2O_{10}P_2$ (1037.06): C, 70.65; H, 5.25; N, 2.70%. Found: C, 70.1; H, 5.3; N, 2.7%. ^{1}H NMR: δ 3.01, 3.02, 3.03, 3.06, 3.13, 3.20, 3.23, 3.31, 3.36, 3.50, 3.51, 3.55, 3.60, 3.61, 3.76 and

3.83 (12 H, 16 s, 4 OCH_3), 4.5–4.8 (2 H, m, NCH_2), 5.13, 5.15, 5.16, 5.57, 5.61, 5.63, 5.64 and 5.66 (2 H, 8 d, $^3J_{PH}$ 20.9, 20.2, 19.5, 19.5, 20.5, 17.6, 19.9 and 19.8 Hz, 2 P—C—CH), 6.1–6.3 (1 H, m, N—CH=CH), 7.1–7.8 (37 H, m, 2 $P(C_6H_5)_3$, $NCH_2C_6H_5$, NC*H*=CH and N—C=CH). ^{13}C NMR: δ 40.12, 41.05, 42.25 and 43.06 (4 d, $^1J_{PC}$ 124.1, 123.1, 126.6, and 134.6 Hz, P=C), 48.38, 48.50, 48.72, 19.40, 49.42, 51.45, 51.55, 51.85, 52.13 and 53.01 (OCH_3), 56.20, 56.34, 56.45 and 56.60 (NCH_2), 60.5–61.5 (P—C—*C*H), 109.03, 109.05, 109.12 and 109.20 (pyrrole C^4H), 123.95, 124.05, 124.21 and 124.34 (pyrrole C^3H), 125.20, 125.52, 125.81 and 126.20 (4 d, $^1J_{PC}$ 92.2, 91.9, 91.9 and 91.0 Hz, C^{ipso}), 126.03, 126.15, 126.59 and 126.67 (pyrrole C^5H), 127.14, 127.29, 127.47 and 127.48 (C^p of CH_2Ph), 127.9–128.6 (C^m, C^o of CH_2Ph and C^m of CH_2Ph), 131–131.8 (pyrrole C^2 and C^p), 132–133.5 (C^o), 168–172 (C=O), 180.05, 180.35, 180.40 and 180.66 (pyrrole-C=O). ^{31}P NMR: δ 24.39, 24.45, 24.98, 25.47 26.04 and 26.06 (Ph_3P^+—C).

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