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Vinyltriphenylphosphonium salt mediated serendipitous synthesis of aryliminophosphoranes

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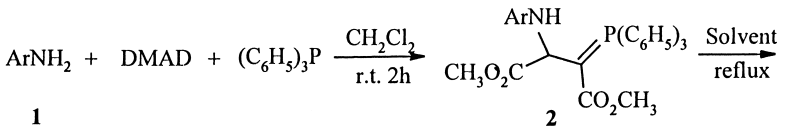
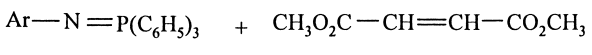
Abstract—Crystalline phosphorus ylides are obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine, dimethyl acetylenedicarboxylate and aromatic amines, such as aniline, 1-naphthylamine, *p*-toluidine, 4-bromoaniline, 4-nitroaniline, 4-acetylaniline, 2-aminopyridine, or 2-amino-5-bromopyridine. These stabilized phosphoranes undergo a smooth intramolecular reaction in boiling *p*-xylene or toluene to produce aryliminophosphoranes in excellent yields. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Iminophosphoranes, compounds of general structure $R_3P{=}NR'$ with four-coordinate phosphorus and incorporating a formal phosphorus–nitrogen double bond, are reactive species, which take part in many valuable reactions in organic synthesis.[1–4] Iminophosphoranes were first reported by Staudinger and Meyer[6] in 1919 but virtually no additional chemistry was reported until the early 1960s. Much chemistry has been discovered in the last three decades with numerous applications to organic synthesis.[1–5] Several methods have been developed for the preparation of iminophosphoranes.[1–10] Reactions of triarylphosphines with dimethyl acetylenedicarboxylate (DMAD), and on occasion, other acetylenic systems have been discussed.[11,12] We report here an efficient synthetic route to aryliminophosphoranes using triphenylphosphine, DMAD, and aromatic amines such as aniline (**a**), 1-naphthylamine (**b**), *p*-toluidine (**c**), 4-bromoaniline (**d**), 4-nitroaniline (**e**), 4-acetylaniline (**f**), 2-aminopyridine (**g**), or 2-amino-5-bromopyridine (**h**). Thus, reaction of aromatic amines **1a–h** with DMAD in the presence of triphenylphosphine leads to the corresponding stable phosphorus ylides **2**, which undergo a smooth transformation in boiling *p*-xylene or toluene to produce iminophosphorane **3**, dimethyl fumarate and dimethyl maleate **4** (see Scheme 1).



1 **2**



3 **4** (*E* and *Z*)

1, 2, 3	Ar	% Yield of 2	% Yield of 3 (from 2)	Solvent
a	Phenyl	98	97	*p*-Xylene
b	1-Naphthyl	98	98	*p*-Xylene
c	4-Methylphenyl	98	98	*p*-Xylene
d	4-Bromophenyl	96	97	Toluene
e	4-Nitrophenyl	98	98	Toluene
f	4-Acetylphenyl	98	97	Toluene
g	2-Pyridyl	98	98	Toluene
h	5-Bromo-2-pyridyl	98	98	Toluene

Scheme 1.

Keywords: aryliminophosphoranes; triphenylphosphine; stable phosphorus ylides; acetylenic esters.

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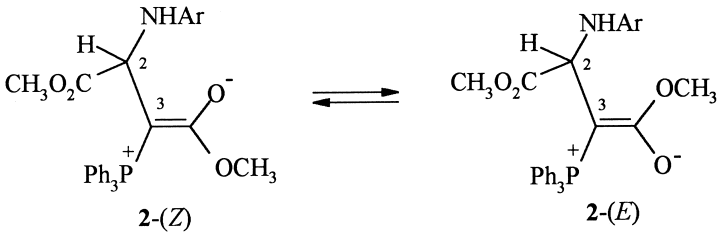
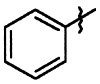
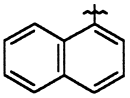
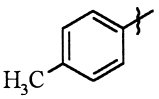
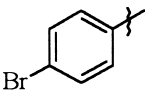
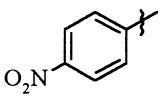
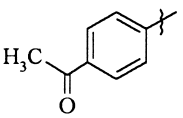
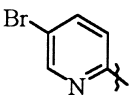
Table 1. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts (δ in ppm) and coupling constants (J in Hz) for H-2, CO_2CH_3, OCH_3, C-2, C-3, and P in the major (M) and minor (m) geometrical isomers of compounds **2a**–**h**



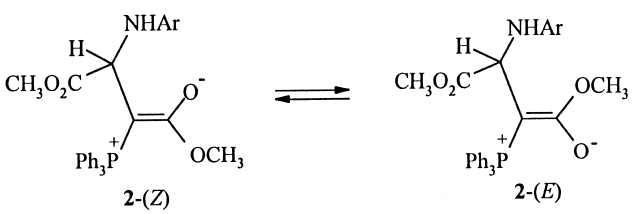
Compound	Ar	Isomer (%)	^{1}H NMR spectroscopic data			^{13}C NMR spectroscopic data		^{31}P
			H-2 ($^{3}J_{PH}$)	OCH_3	CO_2CH_3	C-2 ($^{2}J_{PC}$)	C-3 ($^{1}J_{PC}$)	
2a		M (74) m (26)	4.29 (16.3) 4.16 (16.9)	3.09 3.61	3.68 3.65	56.91 (13.9) 56.21 (15.1)	42.74 (123.4) 44.05 (136.1)	21.93 22.60
2b		M (75) m (25)	4.58 (17.0) 4.39 (16.8)	3.14 3.62	3.69 3.67	56.95 (13.3) 56.43 (13.8)	42.66 (123.6) 44.05 (136.0)	21.77 22.43
2c		M (71) m (29)	4.19 (14.7) 4.11 (15.5)	3.08 3.61	3.68 3.66	57.52 (14.0) 56.74 (12.7)	42.68 (124.0) 43.95 (131.2)	21.91 22.52
2d		M (73) m (27)	4.25 (17.0) 4.09 (17.5)	3.10 3.60	3.68 3.65	56.73 (14.2) 56.10 (15.5)	42.36 (124.1) 43.74 (130.5)	21.74 22.61
2e		M (74) m (26)	4.43 (16.3) 4.23 (17.2)	3.16 3.62	3.70 3.68	55.46 (15.4) 54.95 (16.5)	42.36 (125.3) 43.52 (137.0)	21.64 22.88
2f		M (75) m (25)	4.42 (17.5) 4.24 (17.1)	3.14 3.62	3.68 3.66	55.38 (14.8) 54.85 (14.7)	42.56 (124.9) 43.75 (136.1)	21.80 22.84
2g		M (69) m (31)	4.86 (16.3) 4.67 (17.4)	3.11 3.59	3.68 3.66	53.76 (16.2) 53.33 (15.9)	43.43 (125.9) 44.34 (134.0)	22.50 23.40
2h		M (74) m (26)	4.77 (15.7) 4.66 (17.0)	3.11 3.57	3.68 3.66	53.89 (16.3) 53.37 (16.4)	43.16 (126.0) 44.07 (135.1)	22.51 23.48

2. Results and discussion

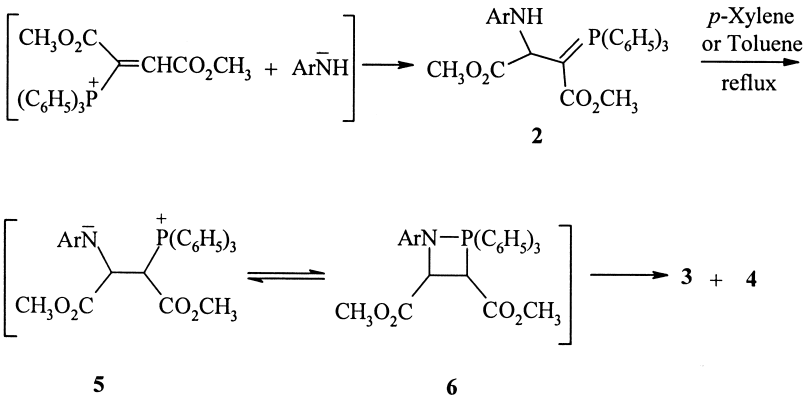
The reaction of aromatic amines **1a**–**h** (see Scheme 1) with DMAD in the presence of triphenylphosphine proceeded spontaneously at room temperature in dichloromethane, and finished within 2 h. ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of phosphorane **2**. Any product other than **2** could not be detected by NMR spectroscopy.

The structures of compounds **2a**–**h** 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. Initial fragmentation involves loss from or complete loss of the side chains.

The ^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **2a**–**h** are consistent with the presence of two isomers. Selected ^{1}H, ^{13}C and ^{31}P NMR chemical shifts and coupling constants of the major (M) and minor (m) geometrical isomers of compounds **2a**–**h** are shown in Table 1. 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*) (see Scheme 2) is slow on the NMR timescale at ambient temperature.



Scheme 2.



Scheme 3.

On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[2,13–19] 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 Michael acceptor is attacked by the nitrogen atom of the conjugate base of the NH-acid to form phosphorane **2** (see Scheme 3).

Phosphorus ylides **2** undergo a smooth, and clean, reaction in boiling *p*-xylene or toluene to produce iminophosphorane **3** and dimethyl fumarate and/or dimethyl maleate (Scheme 1). Structure **3** was assigned to the isolated products on the basis of their elemental analyses and IR, ^{1}H, ^{13}C and ^{31}P NMR and mass spectral data. The mass spectra of iminophosphoranes **3** confirm their molecular weights. Partial assignments of the ^{1}H, ^{13}C and ^{31}P resonances in the ^{1}H, ^{13}C and ^{31}P NMR spectra of **3a–h** are given in Section 3.

Although we have not established the mechanism of the formation of iminophosphoranes **3** from ylides **2** in an experimental manner, it is reasonable to assume that in boiling *p*-xylene or toluene, the NH-proton shifts to the ylidic carbon and forms the phosphorus betaine **5**. This betaine can be in equilibrium with the azaphosphetane. Iminophosphorane **3** is formed from fragmentation of the azaphosphetane **6**. Formation of dimethyl fumarate and/or dimethyl maleate confirms the proposed mechanism (Scheme 3).

In summary, the present synthesis of iminophosphoranes complements older methods[1–10] and offers significant advantages for the synthesis of iminophosphoranes from aromatic amines. The present method carries the advantage that, not only is the reaction performed under neutral conditions, but also that the substances can be mixed without any activation or modification. The procedure described here may be an acceptable method for the preparation of aryliminophosphoranes with variable functionalities.

3. Experimental

Dimethyl acetylenedicarboxylate, triphenylphosphine, aniline, 1-naphthylamine, *p*-toluidine, 4-bromoaniline, 4-nitroaniline, 4-acetylaniline and 2-aminopyridine were obtained from Fluka (Buchs, Switzerland) and were used without further purification. 2-Amino-5-bromopyridine was prepared according to literature.[20] 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 spectrometer at 500.1, 125.8 and 202.5 MHz, respectively. IR spectra were recorded on a Shimadzu IR-460 spectrometer.

3.1. General procedure for preparation of compounds 2a–h

3.1.1. Dimethyl 2-anilino-3-(triphenylphosphoranylidene)butanedioate 2a. The process for the preparation of the title compound is described as an example. To a magnetically stirred solution of triphenylphosphine (0.524 g, 2 mmol) and aniline (0.186 g, 2 mmol) in dichloromethane (4 mL) was added dropwise a mixture of DMAD (0.284 g, 2 mmol) in dichloromethane (2 mL) at −5°C over 10 min. The reaction mixture was then allowed to warm up to room temperature and stirred for 2 h. The solvent was removed under reduced pressure and the residual solid recrystallized from 1:1 hexane–ethyl acetate as pale yellow crystals, mp 192–195°C, 0.97 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 3368 (NH), 1730 and 1613 (C=O). MS, *m/z* (%): 497 (M^+, 6), 435 (20), 405 (8), 383 (29), 303 (10), 262 (100), 183 (37), 78 (20). Anal. Calcd for $C_{30}H_{28}NO_4P$ (497.53): C, 72.42; H, 5.67; N, 2.82. Found: C, 72.4; H, 5.7; N, 2.8%.

Major isomer, **2a**-(*Z*) (74%), ^{1}H NMR: δ 3.09 and 3.68 (6H, 2s, $2OCH_3$), 4.29 (1H, br d, $^{3}J_{PH}$=16.3 Hz, P–C–CH), 5.35 (1H, br, NH), 6.27 (2H, d, *J*=7.5 Hz, 2CH), 7.00 (2H, t, *J*=7.1 Hz, 2CH), 7.08 (1H, t, *J*=7.2 Hz, CH), 7.3–7.6 (15H, m, $3C_6H_5$). ^{13}C NMR: δ 42.74 (d, $^{1}J_{PC}$=123.4 Hz, P=C), 48.85 and 51.94 ($2OCH_3$), 56.91 (d, $^{2}J_{PC}$=13.9 Hz, P–C–*C*H), 115.21 (CH), 117.78 (C), 126.90 (d, $^{1}J_{PC}$=91.8 Hz, C^{ipso}), 128.50 (d, $^{3}J_{PC}$=12.5 Hz, C^{m}), 129.19 (CH), 131.95 (d, $^{4}J_{PC}$=2.3 Hz, C^{p}), 133.80 (d, $^{2}J_{PC}$=9.7 Hz, C^{o}), 147.60 (C–N), 169.73 and 174.66 (2d, $^{2}J_{PC}$=7.7 Hz and $^{3}J_{PC}$=12.8 Hz, 2C=O ester). ^{31}P NMR: δ 21.93 (Ph_3P=C).

Minor isomer, **2a**-(*E*) (26%), ^{1}H NMR: δ 3.61 and 3.65 (6H, 2s, 2OCH$_3$), 4.16 (1H, br d, $^3J_{PH}$=16.9 Hz, P–C–CH), 4.85 (1H, br, NH), 6.18 (2H, d, *J*=7.0 Hz, 2CH), 6.65 (2H, t, *J*=7.0 Hz, 2CH), 6.67 (1H, t, *J*=7.1 Hz, CH), 7.3–7.6 (15H, m, 3C$_6$H$_5$). ^{13}C NMR: δ 44.05 (d, $^1J_{PC}$=136.1 Hz, P=C), 50.08 and 51.85 (2OCH$_3$), 56.21 (d, $^2J_{PC}$=15.1 Hz, P–C–*C*H), 115.07 (CH), 117.91 (C), 126.33 (d, $^1J_{PC}$=90.6 Hz, C^{ipso}), 128.54 (d, $^3J_{PC}$=12.2 Hz, C^m), 129.12 (CH), 131.90 (d, $^4J_{PC}$=2.2 Hz, C^p), 133.74 (d, $^2J_{PC}$=9.6 Hz, C^o), 147.54 (C–N), 170.01 and 174.60 (2d, $^2J_{PC}$=7.6 Hz and $^3J_{PC}$=14.5 Hz, 2C=O ester). ^{31}P NMR: δ 22.60 (Ph$_3$P=C).

3.1.2. Dimethyl 2-(1-naphthylamino)-3-(triphenylphosphoranylidene) butanedioate 2b. Pale yellow crystals, mp 180–183°C, 1.07 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 3390 (NH), 1730, 1614 (C=O). MS, *m*/*z* (%): 547 (M$^+$, 3), 485 (14), 459 (10), 405 (8), 262 (100), 183 (66), 108 (42), 78 (36), 51 (31). Anal. Calcd for $C_{34}H_{30}NO_4P$ (547.59): C, 74.58; H, 5.52; N, 2.56. Found: C, 74.6; H, 5.5; N, 2.6%.

Major isomer, **2b**-(*Z*) (75%), ^{1}H NMR: δ 3.14 and 3.69 (6H, 2s, 2OCH$_3$), 4.58 (1H, dd, $^3J_{PH}$=17.0 Hz and $^3J_{HH}$=7.0 Hz, P–C–CH), 6.18 (2H, br, NH and CH), 7.15 (2H, br, 2CH), 7.3–7.6 (17H, m, 3C$_6$H$_5$ and 2CH), 7.70 (1H, d, *J*=8.0 Hz, CH), 7.84 (1H, d, *J*=8.0 Hz, CH). ^{13}C NMR: δ 42.66 (d, $^1J_{PC}$=123.6 Hz, P=C), 48.96 and 51.99 (2OCH$_3$), 56.95 (d, $^2J_{PC}$=13.3 Hz, P–C–*C*H), 107.29, 117.44, 121.31 and 124.31 (4CH), 124.99 (d, $^1J_{PC}$=91.1 Hz, C^{ipso}), 125.35 (CH), 126.32 and 127.10 (2C), 128.14 (CH), 128.44 (d, $^3J_{PC}$=12.1 Hz, C^m), 131.91 (d, $^4J_{PC}$=2.0 Hz, C^p), 133.68 (d, $^2J_{PC}$=9.8 Hz, C^o), 134.42 (CH), 142.86 (C–N), 170.00 and 174.75 (2d, $^2J_{PC}$=6.5 Hz and $^3J_{PC}$=12.1 Hz, 2C=O ester). ^{31}P NMR: δ 21.77 (Ph$_3$P=C).

Minor isomer, **2b**-(*E*) (25%), ^{1}H NMR: δ 3.62 and 3.67 (6H, 2s, 2OCH$_3$), 4.39 (1H, dd, $^3J_{PH}$=16.8 Hz and $^3J_{HH}$=7.0 Hz, P–C–CH), 5.68 (1H, br d, *J*=7.0 Hz, NH), 5.96 (1H, br d, *J*=7.5 Hz, CH), 7.07 (1H, br t, *J*=7.0 Hz, CH), 7.13 (1H, br t, *J*=6.9 Hz, CH), 7.2–7.6 (17H, m, 3C$_6$H$_5$ and 2CH), 7.74 (1H, d, *J*=8.0 Hz, CH), 7.79 (1H, d, *J*=8.0 Hz, CH). ^{13}C NMR: δ 44.05 (d, $^1J_{PC}$=136.0 Hz, P=C), 50.14 and 51.92 (2OCH$_3$), 56.43 (d, $^2J_{PC}$=13.8 Hz, P–C–*C*H), 107.14, 117.65, 120.74 and 124.38 (4CH), 126.18 (d, $^1J_{PC}$=93.5 Hz, C^{ipso}), 125.30 (CH), 126.30 and 127.12 (2C), 128.10 (CH), 128.46 (d, $^3J_{PC}$=12.1 Hz, C^m), 131.90 (d, $^4J_{PC}$=2.0 Hz, C^p), 133.70 (d, $^2J_{PC}$=9.8 Hz, C^o), 134.35 (CH), 142.74 (C–N), 170.25 and 174.70 (2d, $^2J_{PC}$=6.4 Hz and $^3J_{PC}$=12.0 Hz, 2C=O ester). ^{31}P NMR: δ 22.43 (Ph$_3$P=C).

3.1.3. Dimethyl 2-(4-methylanilino)-3-(triphenylphosphoranylidene)butanedioate 2c. Pale yellow crystals, mp 180–183°C, 1.00 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 3410 (NH), 1731, 1596 (C=O). MS, *m*/*z* (%): 511 (M$^+$, 9), 459 (10), 449 (13), 405 (10), 262 (100), 183 (49), 108 (51), 78 (44), 51 (39). Anal. Calcd for $C_{31}H_{30}NO_4P$ (511.56): C, 72.79; H, 5.91; N, 2.74. Found: C, 72.8; H, 5.9; N, 2.7%.

Major isomer, **2c**-(*Z*) (71%), ^{1}H NMR: δ 2.20 (3H, s, CH$_3$), 3.08 and 3.68 (6H, 2s, 2OCH$_3$), 4.19 (1H, dd, $^3J_{PH}$=14.7 Hz and $^3J_{HH}$=7.0 Hz, P–C–CH), 5.28 (1H, br d, $^3J_{HH}$=7.0 Hz, NH), 6.20 (2H, d, *J*=7.7 Hz, 2CH), 6.82 (2H, d, *J*=7.7 Hz, 2CH), 7.3–7.6 (15H, m, 3C$_6$H$_5$). ^{13}C NMR: δ 20.47 (CH$_3$), 42.68 (d, $^1J_{PC}$=124.0 Hz, P=C), 48.79 and 51.87 (2OCH$_3$), 57.52 (d, $^2J_{PC}$=14.0 Hz, P–C–*C*H), 115.80 (CH), 126.95 (d, $^1J_{PC}$=91.4 Hz, C^{ipso}), 127.06 (C), 128.45 (d, $^3J_{PC}$=12.3 Hz, C^m), 129.26 (CH), 131.89 (C^p), 133.77 (d, $^2J_{PC}$=9.6 Hz, C^o), 145.40 (C–N), 169.58 and 174.72 (2d, $^2J_{PC}$=7.9 Hz and $^3J_{PC}$=12.6 Hz, 2C=O ester). ^{31}P NMR: δ 21.91 (Ph$_3$P=C).

Minor isomer, **2c**-(*E*) (29%), ^{1}H NMR: δ 2.22 (3H, s, CH$_3$), 3.61 and 3.66 (6H, 2s, 2OCH$_3$), 4.11 (1H, dd, $^3J_{PH}$=15.5 Hz and $^3J_{HH}$=6.9 Hz, P–C–CH), 4.77 (1H, br d, $^3J_{HH}$=6.9 Hz, NH), 6.11 (2H, d, *J*=7.3 Hz, 2CH), 6.84 (2H, d, *J*=7.3 Hz, 2CH), 7.3–7.6 (15H, m, 3C$_6$H$_5$). ^{13}C NMR: δ 20.43 (CH$_3$), 43.95 (d, $^1J_{PC}$=131.2 Hz, P=C), 50.02 and 51.86 (2OCH$_3$), 56.74 (d, $^2J_{PC}$=12.7 Hz, P–C–*C*H), 115.71 (CH), 126.36 (d, $^1J_{PC}$=91.8 Hz, C^{ipso}), 127.25 (C), 128.55 (d, $^3J_{PC}$=12.2 Hz, C^m), 129.24 (CH), 131.88 (C^p), 133.72 (d, $^2J_{PC}$=9.6 Hz, C^o), 145.26 (C–N), 170.34 and 174.65 (2d, $^2J_{PC}$=7.8 Hz and $^3J_{PC}$=14.5 Hz, 2C=O ester). ^{31}P NMR: δ 22.52 (Ph$_3$P=C).

3.1.4. Dimethyl 2-(4-bromoanilino)-3-(triphenylphosphoranylidene)butanedioate 2d. Pale orange crystals, mp 178–181°C, 1.01 g, yield 96%. IR (KBr) (ν_{max}/cm^{-1}): 3365 (NH), 1728, 1609 (C=O). MS, *m*/*z* (%): 577 (M$^+$+2, 9), 575 (M$^+$, 11), 405 (14), 262 (100), 183 (72), 108 (49), 79 (36). Anal. Calcd for $C_{30}H_{27}BrNO_4P$ (576.43): C, 62.51; H, 4.72; N, 2.43. Found: C, 62.6; H, 4.7; N, 2.5%.

Major isomer, **2d**-(*Z*) (73%), ^{1}H NMR: δ 3.10 and 3.68 (6H, 2s, 2OCH$_3$), 4.25 (1H, dd, $^3J_{PH}$=17.0 Hz and $^3J_{HH}$=7.9 Hz, P–C–CH), 5.36 (1H, br d, $^3J_{HH}$=7.9 Hz, NH), 6.15 (2H, d, *J*=8.0 Hz, 2CH), 7.09 (2H, d, *J*=8.0 Hz, 2CH), 7.3–7.6 (15H, m, 3C$_6$H$_5$). ^{13}C NMR: δ 42.36 (d, $^1J_{PC}$=124.1 Hz, P=C), 48.88 and 51.97 (2OCH$_3$), 56.73 (d, $^2J_{PC}$=14.2 Hz, P–C–*C*H), 109.25 (C–Br), 116.61 (CH), 126.65 (d, $^1J_{PC}$=91.8 Hz, C^{ipso}), 128.50 (d, $^3J_{PC}$=12.3 Hz, C^m), 131.42 (CH), 132.01 (d, $^4J_{PC}$=2.1 Hz, C^p), 133.63 (d, $^2J_{PC}$=9.8 Hz, C^o), 146.56 (C–N), 169.72 and 174.23 (2d, $^2J_{PC}$=6.6 Hz and $^3J_{PC}$=12.8 Hz, 2C=O ester). ^{31}P NMR: δ 21.74 (Ph$_3$P=C).

Minor isomer, **2d**-(*E*) (27%), ^{1}H NMR: δ 3.60 and 3.65 (6H, 2s, 2OCH$_3$), 4.09 (1H, br d, $^3J_{PH}$=17.5 Hz, P–C–CH), 4.85 (1H, br, NH), 6.05 (2H, d, *J*=7.9 Hz, 2CH), 7.05 (2H, d, *J*=7.9 Hz, 2CH), 7.3–7.6 (15H, m, 3C$_6$H$_5$). ^{13}C NMR: δ 43.74 (d, $^1J_{PC}$=130.5 Hz, P=C), 50.06 and 51.94 (2OCH$_3$), 56.10 (d, $^2J_{PC}$=15.5 Hz, P–C–*C*H), 109.22 (C–Br), 116.31 (CH), 126.12 (d, $^1J_{PC}$=90.7 Hz, C^{ipso}), 128.58 (d, $^3J_{PC}$=12.3 Hz, C^m), 131.40 (CH), 132.06 (d, $^4J_{PC}$=2.0 Hz, C^p), 133.60 (d, $^2J_{PC}$=9.7 Hz, C^o), 146.46 (C–N), 170.20 and 174.15 (2d, $^2J_{PC}$=6.6 Hz and $^3J_{PC}$=14.1 Hz, 2C=O ester). ^{31}P NMR: δ 22.61 (Ph$_3$P=C).

3.1.5. Dimethyl 2-(4-nitroanilino)-3-(triphenylphosphoranylidene)butanedioate 2e. Pale yellow crystals, mp 209–211°C, 1.06 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 3370 (NH), 1723, 1608, 1586 (C=O). MS, *m*/*z* (%): 542 (M$^+$, 2), 530 (5), 483 (100), 451 (20), 405 (74), 303 (20), 262 (60), 183 (45), 108 (32). Anal. Calcd for $C_{30}H_{27}N_2O_6P$ (542.53): C, 66.42; H, 5.02; N, 5.16. Found: C, 66.5; H, 5.1; N, 5.1%.

Major isomer, **2e**-(*Z*) (74%), ^{1}H NMR: δ 3.16 and 3.70 (6H, 2s, 2OCH$_3$), 4.43 (1H, dd, $^3J_{PH}$=16.3 Hz and $^3J_{HH}$=8.0 Hz, P–C–CH), 6.08 (1H, d, $^3J_{HH}$=8.0 Hz, NH), 6.15 (2H, d, *J*=8.5 Hz, 2CH), 7.4–7.7 (15H, m, 3C$_6$H$_5$), 7.93 (2H, d, *J*=8.5 Hz, 2CH). ^{13}C NMR: δ 42.36 (d, $^1J_{PC}$=125.3 Hz, P=C), 49.21 and 52.36 (2OCH$_3$), 55.46 (d, $^2J_{PC}$=15.4 Hz, P–C–*C*H), 111.68 (CH), 126.12 (CH), 126.27 (d, $^1J_{PC}$=92.0 Hz, C^{ipso}), 128.80 (d, $^3J_{PC}$=12.2 Hz, C^m), 132.40 (C^p), 133.62 (d, $^2J_{PC}$=9.4 Hz, C^o), 137.62 and 152.33 (2C–N), 170.15 and 173.46 (2d, $^2J_{PC}$=6.9 Hz and $^3J_{PC}$=12.2 Hz, 2C=O ester). ^{31}P NMR: δ 21.64 (Ph$_3$P=C).

Minor isomer, **2e**-(*E*) (26%), ^{1}H NMR: δ 3.62 and 3.68 (6H, 2s, 2OCH$_3$), 4.23 (1H, dd, $^3J_{PH}$=17.2 Hz and $^3J_{HH}$=8.0 Hz, P–C–CH), 5.57 (1H, d, $^3J_{HH}$=8.0 Hz, NH), 6.10 (2H, d, *J*=8.5 Hz, 2CH), 7.4–7.7 (15H, m, 3C$_6$H$_5$), 7.91 (2H, d, *J*=8.5 Hz, 2CH). ^{13}C NMR: δ 43.52 (d, $^1J_{PC}$=137.0 Hz, P=C), 50.30 and 52.33 (2OCH$_3$), 54.95 (d, $^2J_{PC}$=16.5 Hz, P–C–*C*H), 111.44 (CH), 125.91 (d, $^1J_{PC}$=92.0 Hz, C^{ipso}), 126.14 (CH), 128.82 (d, $^3J_{PC}$=12.1 Hz, C^m), 132.42 (C^p), 133.64 (d, $^2J_{PC}$=9.5 Hz, C^o), 137.65 and 152.31 (2C–N), 170.12 and 173.42 (2d, $^2J_{PC}$=7.0 Hz and $^3J_{PC}$=12.4 Hz, 2C=O ester). ^{31}P NMR: δ 22.88 (Ph$_3$P=C).

3.1.6. Dimethyl 2-(4-acetylanilino)-3-(triphenylphosphoranylidene)butanedioate 2f. Pale orange crystals, mp 169–171°C, 1.06 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 3355 (NH), 1731, 1603 (C=O). MS, *m/z* (%): 539 (M$^+$, 2), 459 (8), 405 (5), 262 (100), 183 (75), 108 (47), 51 (42). Anal. Calcd for C$_{32}$H$_{30}$NO$_5$P (539.57): C, 71.23; H, 5.60; N, 2.60. Found: C, 71.4; H, 5.6; N, 2.5%.

Major isomer, **2f**-(*Z*) (75%), ^{1}H NMR: δ 2.45 (3H, s, CH$_3$), 3.14 and 3.68 (6H, 2s, 2OCH$_3$), 4.42 (1H, dd, $^3J_{PH}$=17.5 Hz and $^3J_{HH}$=8.3 Hz, P–C–CH), 5.82 (1H, br d, $^3J_{HH}$=8.3 Hz, NH), 6.21 (2H, d, *J*=7.9 Hz, 2CH), 7.4–7.6 (15H, m, 3C$_6$H$_5$), 7.68 (2H, d, *J*=7.9 Hz, 2CH). ^{13}C NMR: δ 25.91 (CH$_3$), 42.56 (d, $^1J_{PC}$=124.9 Hz, P=C), 49.04 and 52.14 (2OCH$_3$), 55.38 (d, $^2J_{PC}$=14.8 Hz, P–C–*C*H), 112.29 (CH), 126.43 (C), 126.44 (d, $^1J_{PC}$=92.0 Hz, C^{ipso}), 128.67 (d, $^3J_{PC}$=12.1 Hz, C^m), 130.43 (CH), 132.22 (C^p), 133.62 (d, $^2J_{PC}$=9.4 Hz, C^o), 151.31 (C–N), 169.97 and 173.90 (2d, $^2J_{PC}$=7.4 Hz and $^3J_{PC}$=12.6 Hz, 2C=O ester), 196.19 (C=O). ^{31}P NMR: δ 21.80 (Ph$_3$P=C).

Minor isomer, **2f**-(*E*) (25%), ^{1}H NMR: δ 2.47 (3H, s, CH$_3$), 3.62 and 3.66 (6H, 2s, 2OCH$_3$), 4.24 (1H, dd, $^3J_{PH}$=17.1 Hz and $^3J_{HH}$=8.3 Hz, P–C–CH), 5.34 (1H, d, $^3J_{HH}$=8.3 Hz, NH), 6.14 (2H, d, *J*=7.7 Hz, 2CH), 7.4–7.6 (15H, m, 3C$_6$H$_5$), 7.66 (2H, d, *J*=7.7 Hz, 2CH). ^{13}C NMR: δ 25.89 (CH$_3$), 43.75 (d, $^1J_{PC}$=136.1 Hz, P=C), 50.17 and 52.12 (2OCH$_3$), 54.85 (d, $^2J_{PC}$=14.7 Hz, P–C–*C*H), 112.05 (CH), 125.96 (d, $^1J_{PC}$=92.0 Hz, C^{ipso}), 126.45 (C), 128.69 (d, $^3J_{PC}$=12.1 Hz, C^m), 130.41 (CH), 132.21 (C^p), 133.65 (d, $^2J_{PC}$=9.4 Hz, C^o), 151.29 (C–N), 170.05 and 173.88 (2d, $^2J_{PC}$=7.3 Hz and $^3J_{PC}$=12.6 Hz, 2C=O ester), 196.15 (C=O). ^{31}P NMR: δ 22.84 (Ph$_3$P=C).

3.1.7. Dimethyl 2-(2-pyridylamino)-3-(triphenylphosphoranylidene)butanedioate 2g. Pale yellow crystals, mp 196–198°C, 0.98 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 3370 (NH), 1730 and 1608 (C=O). MS, *m/z* (%): 498 (M$^+$, 4), 439 (100), 407 (40), 354 (10), 303 (15), 262 (55), 183 (34), 78 (20). Anal. Calcd for C$_{29}$H$_{27}$N$_2$O$_4$P (498.52): C, 69.87; H, 5.46; N, 5.62. Found: C, 69.9; H, 5.5; N, 5.6%.

Major isomer, **2g**-(*Z*) (69%), ^{1}H NMR: δ 3.11 and 3.68 (6H, 2s, 2OCH$_3$), 4.86 (1H, dd, $^3J_{PH}$=16.3 Hz and $^3J_{HH}$=9.2 Hz, P–C–CH), 6.15 (1H, d, $^3J_{HH}$=9.2 Hz, NH), 6.40 (2H, m, 2CH), 7.25 (1H, m, CH), 7.4–7.7 (15H, m, 3C$_6$H$_5$), 7.66 (1H, d, *J*=7.7 Hz, CH). ^{13}C NMR: δ 43.43 (d, $^1J_{PC}$=125.9 Hz, P=C), 48.86 and 52.01 (2OCH$_3$), 53.76 (d, $^2J_{PC}$=16.2 Hz, P–C–*C*H), 109.15 and 112.37 (2CH), 127.07 (d, $^1J_{PC}$=92.1 Hz, C^{ipso}), 128.42 (d, $^3J_{PC}$=12.3 Hz, C^m), 131.86 (C^p), 133.82 (d, $^2J_{PC}$=9.8 Hz, C^o), 136.54 and 147.24 (2CH), 157.91 (N=C–N), 170.15 and 174.81 (2d, $^2J_{PC}$=8.3 Hz and $^3J_{PC}$=13.0 Hz, 2C=O ester). ^{31}P NMR: δ 22.50 (Ph$_3$P=C).

Minor isomer, **2g**-(*E*) (31%), ^{1}H NMR: δ 3.59 and 3.66 (6H, 2s, 2OCH$_3$), 4.67 (1H, dd, $^3J_{PH}$=17.4 Hz and $^3J_{HH}$=9.1 Hz, P–C–CH), 5.58 (1H, d, $^3J_{HH}$=9.1 Hz, NH), 6.12 (1H, d, *J*=7.5 Hz, CH), 6.42 (1H, m, CH), 7.23 (1H, m, CH), 7.4–7.7 (15H, m, 3C$_6$H$_5$), 7.76 (1H, d, *J*=7.6 Hz, CH). ^{13}C NMR: δ 44.34 (d, $^1J_{PC}$=134.0 Hz, P=C), 50.08 and 51.99 (2OCH$_3$), 53.33 (d, $^2J_{PC}$=15.9 Hz, P–C–*C*H), 107.95 and 112.53 (2CH), 126.45 (d, $^1J_{PC}$=91.3 Hz, C^{ipso}), 128.58 (d, $^3J_{PC}$=12.7 Hz, C^m), 131.84 (C^p), 133.80 (d, $^2J_{PC}$=9.5 Hz, C^o), 136.70 and 147.53 (2CH), 157.76 (N=C–N), 170.44 and 174.79 (2d, $^2J_{PC}$=8.5 Hz and $^3J_{PC}$=18.1 Hz, 2C=O ester). ^{31}P NMR: δ 23.40 (Ph$_3$P=C).

3.1.8. Dimethyl 2-(5-bromo-2-pyridylamino)-3-(triphenylphosphoranylidene) butanedioate 2h. Pale orange crystals, mp 197–199°C, 1.13 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 3385 (NH), 1713 and 1612 (C=O). MS, *m/z* (%): 578 (M$^+$+2, 6), 576 (M$^+$, 8), 519 (65), 487 (25), 434 (21), 383 (24), 262 (100), 183 (42), 78 (35). Anal. Calcd for C$_{29}$H$_{26}$BrN$_2$O$_4$P (577.41): C, 60.32; H, 4.54; N, 4.85. Found: C, 60.3; H, 4.5; N, 4.9%.

Major isomer, **2h**-(*Z*) (74%), ^{1}H NMR: δ 3.11 and 3.68 (6H, 2s, 2OCH$_3$), 4.77 (1H, dd, $^3J_{PH}$=15.7 Hz and $^3J_{HH}$=9.0 Hz, P–C–CH), 6.27 (1H, d, $^3J_{HH}$=9.0 Hz, NH), 6.31 (1H, d, $^3J_{HH}$=8.7 Hz, CH), 7.31 (1H, d, $^3J_{HH}$=8.7 Hz, CH), 7.4–7.6 (15H, m, 3C$_6$H$_5$), 7.66 (1H, s, CH). ^{13}C NMR: δ 43.16 (d, $^1J_{PC}$=126.0 Hz, P=C), 48.93 and 52.09 (2OCH$_3$), 53.89 (d, $^2J_{PC}$=16.3 Hz, P–C–*C*H), 106.59 (CH), 110.80 (C–Br), 126.89 (d, $^1J_{PC}$=92.1 Hz, C^{ipso}), 128.53 (d, $^3J_{PC}$=12.3 Hz, C^m), 132.00 (C^p), 133.80 (d, $^2J_{PC}$=9.8 Hz, C^o), 138.92 and 147.67 (2CH), 156.46 (N=C–N), 170.15 and 174.45 (2d, $^2J_{PC}$=8.4 Hz and $^3J_{PC}$=13.2 Hz, 2C=O ester). ^{31}P NMR: δ 22.51 (Ph$_3$P=C).

Minor isomer, **2h**-(*E*) (26%), ^{1}H NMR: δ 3.57 and 3.66 (6H, 2s, 2OCH$_3$), 4.66 (1H, dd, $^3J_{PH}$=17.0 Hz and $^3J_{HH}$=8.9 Hz, P–C–CH), 5.67 (1H, d, $^3J_{HH}$=8.9 Hz, NH), 6.13 (1H, d, $^3J_{HH}$=8.2 Hz, CH), 7.29 (1H, d, $^3J_{HH}$=8.2 Hz, CH), 7.4–7.6 (15H, m, 3C$_6$H$_5$), 7.72 (1H, s, CH). ^{13}C NMR: δ 44.07 (d, $^1J_{PC}$=135.1 Hz, P=C), 50.11 and 52.05 (2OCH$_3$), 53.37 (d, $^2J_{PC}$=16.4 Hz, P–C–*C*H), 106.65 (CH), 109.81 (C–Br), 126.33 (d, $^1J_{PC}$=92.8 Hz, C^{ipso}), 128.65 (d, $^3J_{PC}$=12.2 Hz, C^m), 132.02 (C^p), 133.82 (d, $^2J_{PC}$=9.5 Hz, C^o), 138.95 and 147.75 (2CH), 156.28 (N=C–N), 170.25 and 174.50 (2d, $^2J_{PC}$=8.3 Hz and $^3J_{PC}$=12.9 Hz, 2C=O ester). ^{31}P NMR: δ 23.48 (Ph$_3$P=C).

3.2. General procedure for preparation of compounds 3a–h

3.2.1. *N*-Phenyltriphenyliminophosphorane 3a. The process for the preparation of **3a** is described as an example. A mixture of **2a** (0.50 g, 1 mmol) in *p*-xylene (10 mL) was refluxed for 10 h. The solvent was removed under reduced pressure. Dimethyl fumarate sublimated under reduced pressure and the residue recrystallised from 1:1 hexane–ethyl acetate as colorless crystals, mp 131–133°C (Lit.[21] 133–134°C), 0.34 g, yield 97%. IR (KBr) (ν_{max}/cm^{-1}): 1577, 1473, 1328, 1103, 747, 711, 688, 563, 517. MS, *m*/*z* (%): 353 (M$^+$, 100), 277 (71), 183 (42), 78 (51). Anal. Calcd for $C_{24}H_{20}NP$ (353.40): C, 81.57; H, 5.70; N, 3.96. Found: C, 81.6; H, 5.7; N, 4.0%. ^{1}H NMR: δ 6.64 (1H, t, J=7.2 Hz, CH), 6.80 (2H, d, J=8.0 Hz, 2CH), 7.00 (2H, dd, J=7.2, 8.0 Hz, 2CH), 7.42 (6H, td, $^3J_{HH}$=7.7 Hz and $^4J_{PH}$=2.9 Hz, 6*meta*CH), 7.49 (3H, dt, $^3J_{HH}$=7.7 Hz and $^5J_{PH}$=1.5 Hz, 3*para* CH), 7.74 (6H, dd, $^3J_{HH}$=7.7 Hz and $^3J_{PH}$=12.0 Hz, 6*ortho*CH). ^{13}C NMR: δ 117.31 (CH), 123.46 (d, $^3J_{PC}$=17.5 Hz, CH), 128.55 (d, $^3J_{PC}$=12.2 Hz, C^m), 128.58 (CH), 131.15 (d, $^1J_{PC}$=98.9 Hz, C^{ipso}), 131.61 (d, $^4J_{PC}$=2.6 Hz, C^p), 132.61 (d, $^2J_{PC}$=9.6 Hz, C^o), 151.12 (d, $^2J_{PC}$=2.1 Hz, C–N=P). ^{31}P NMR: δ 3.11 (Ph_3P=N).

3.2.2. *N*-1-Naphthyltriphenyliminophosphorane 3b. Colorless crystals, mp 110–112°C (from 1:1 hexane–ethyl acetate), 0.40 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 1555, 1443, 1392, 1323, 1115, 711, 519. MS, *m*/*z* (%): 403 (M$^+$, 100), 277 (84), 183 (25), 128 (28), 78 (20). Anal. Calcd for $C_{28}H_{22}NP$ (403.46): C, 83.36; H, 5.50; N, 3.47. Found: C, 83.4; H, 5.6; N, 3.5%. ^{1}H NMR: δ 6.43 (1H, d, J=7.4 Hz, CH), 6.99 (1H, t, J=7.8 Hz, CH), 7.13 (1H, d, J=8.1 Hz, CH), 7.42 (7H, m, 6*meta*CH and CH), 7.49 (4H, m, 3*para*CH and CH), 7.71 (1H, d, J=7.8 Hz, CH), 7.83 (6H, dd, $^3J_{HH}$=8.0 Hz and $^3J_{PH}$=11.9 Hz, 6*ortho*CH), 8.91 (1H, d, J=8.1 Hz, CH). ^{13}C NMR: δ 114.12 (d, $^3J_{PC}$=10.6 Hz, CH), 116.70, 123.73, 125.44, 125.46, 126.23 and 127.40 (6CH), 128.60 (d, $^3J_{PC}$=12.2 Hz, C^m), 131.17 (d, $^1J_{PC}$=99.6 Hz, C^{ipso}), 131.66 (d, $^4J_{PC}$=2.6 Hz, C^p), 131.98 (d, $^3J_{PC}$=22.1 Hz, C), 132.64 (d, $^2J_{PC}$=9.6 Hz, C^o), 135.06 (d, $^4J_{PC}$=2.6 Hz, C), 148.01 (C–N=P). ^{31}P NMR: δ 3.45 (Ph_3P=N).

3.2.3. *N*-(4-Methylphenyl)triphenyliminophosphorane 3c. Colorless crystals, mp 137–139°C (from 1:1 hexane–ethyl acetate) (Lit.[21] 136–137°C), 0.36 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 1595, 1494, 1426, 1323, 1103, 813, 711, 518. MS, *m*/*z* (%): 367 (M$^+$, 100), 277 (62), 183 (45), 91 (18), 78 (33). Anal. Calcd for $C_{25}H_{22}NP$ (367.43): C, 81.72; H, 6.04; N, 3.81. Found: C, 81.7; H, 6.0; N, 3.8%. ^{1}H NMR: δ 2.15 (3H, s, CH_3), 6.73 (2H, d, J=8.0 Hz, 2CH), 6.80 (2H, d, J=8.0 Hz, 2CH), 7.36 (6H, dt, $^3J_{HH}$=7.9 Hz and $^4J_{PH}$=2.9 Hz, 6*meta*CH), 7.43 (3H, dt, $^3J_{HH}$=7.9 Hz and $^5J_{PH}$=1.3 Hz, 3*para*CH), 7.73 (6H, dd, $^3J_{HH}$=7.9 Hz and $^3J_{PH}$=11.7 Hz, 6*ortho*CH). ^{13}C NMR: δ 20.49 (CH_3), 123.17 (d, $^3J_{PC}$=17.4 Hz, CH), 126.19 (*C*–CH_3), 128.48 (d, $^3J_{PC}$=11.9 Hz, C^m), 129.20 (CH), 131.20 (d, $^1J_{PC}$=98.6 Hz, C^{ipso}), 131.52 (d, $^4J_{PC}$=2.5 Hz, C^p), 132.54 (d, $^2J_{PC}$=9.6 Hz, C^o), 148.30 (d, $^2J_{PC}$=2.6 Hz, C–N=P). ^{31}P NMR: δ 3.02 (Ph_3P=N).

3.2.4. *N*-(4-Bromophenyl)triphenyliminophosphorane 3d. Colorless crystals, mp 125–126°C (from 1:1 hexane–ethyl acetate) (Lit.[21] 126–127°C), 0.42 g, yield 97%. IR (KBr) (ν_{max}/cm^{-1}): 1565, 1469, 1305, 1102, 818. MS, *m*/*z* (%): 433 (M$^+$+2, 86), 431 (M$^+$, 90), 277 (100), 183 (49), 156 (45), 78 (20). Anal. Calcd for $C_{24}H_{19}BrNP$ (432.30): C, 66.68; H, 4.43; N, 3.24. Found: C, 66.7; H, 4.4; N, 3.2%. ^{1}H NMR: δ 6.65 (2H, d, J=8.2 Hz, 2CH), 7.05 (2H, d, J=8.2 Hz, 2CH), 7.42 (6H, dt, $^3J_{HH}$=7.7 Hz and $^4J_{PH}$=3.0 Hz, 6*meta*CH), 7.49 (3H, dt, $^3J_{HH}$=7.7 Hz and $^5J_{PH}$=1.3 Hz, 3*para*CH), 7.72 (6H, dd, $^3J_{HH}$=7.7 Hz and $^3J_{PH}$=11.6 Hz, 6*ortho*CH). ^{13}C NMR: δ 109.27 (C–Br), 124.94 (d, $^3J_{PC}$=17.6 Hz, CH), 128.63 (d, $^3J_{PC}$=12.1 Hz, C^m), 130.56 (d, $^1J_{PC}$=99.4 Hz, C^{ipso}), 131.28 (CH), 131.78 (d, $^4J_{PC}$=1.8 Hz, C^p), 132.48 (d, $^2J_{PC}$=9.6 Hz, C^o), 150.45 (d, $^2J_{PC}$=1.9 Hz, C–N=P). ^{31}P NMR: δ 4.22 (Ph_3P=N).

3.2.5. *N*-(4-Nitrophenyl)triphenyliminophosphorane 3e. Pale yellow crystals, mp 155–157°C (from ether) (Lit.[21] 158–159°C), 0.39 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 1570, 1488, 1378, 1209, 1099. MS, *m*/*z* (%): 398 (M$^+$, 100), 351 (25), 321 (8), 277 (30), 262 (20), 183 (85), 152 (20), 108 (30), 77 (25). Anal. Calcd for $C_{24}H_{19}N_2O_2P$ (398.40): C, 72.36; H, 4.81; N, 7.03. Found: C, 72.4; H, 4.7; N, 7.0%. ^{1}H NMR: δ 6.68 (2H, d, $^3J_{HH}$=9.2 Hz, 2CH), 7.48 (6H, td, $^3J_{HH}$=7.6 Hz and $^4J_{PH}$=3.0 Hz, 6*meta*CH), 7.57 (3H, dt, $^3J_{HH}$=7.6 Hz and $^5J_{PH}$=1.4 Hz, 3*para*CH), 7.73 (6H, dd, $^3J_{HH}$=7.6 Hz and $^3J_{PH}$=12.2 Hz, 6*ortho*CH), 7.90 (2H, d, $^3J_{HH}$=9.2 Hz, 2CH). ^{13}C NMR: δ 122.20 (d, $^3J_{PC}$=19.0 Hz, CH), 125.50 (CH), 128.83 (d, $^3J_{PC}$=12.1 Hz, C^m), 129.13 (d, $^1J_{PC}$=100.0 Hz, C^{ipso}), 132.14 (d, $^4J_{PC}$=2.9 Hz, C^p), 132.56 (d, $^2J_{PC}$=9.7 Hz, C^o), 137.97 (C), 160.05 (d, $^2J_{PC}$=2.5 Hz, C–N=P). ^{31}P NMR: δ 7.72 (Ph_3P=N).

3.2.6. *N*-(4-Acetylphenyl)triphenyliminophosphorane 3f. Colorless crystals, mp 127–130°C (from ether), 0.38 g, yield 97%. IR (KBr) (ν_{max}/cm^{-1}): 1646, 1577, 1494, 1347, 1263, 1173, 1102. MS, *m*/*z* (%): 395 (M$^+$, 45), 380 (8), 277 (100), 183 (25), 152 (10), 135 (40), 120 (80), 92 (50), 77 (30). Anal. Calcd for $C_{26}H_{22}NOP$ (395.44): C, 78.97; H, 5.61; N, 3.54. Found: C, 78.8; H, 5.6; N, 3.5%. ^{1}H NMR: δ 2.45 (3H, s, CH_3), 6.76 (2H, d, $^3J_{HH}$=8.7 Hz, 2CH), 7.47 (6H, dt, $^3J_{HH}$=7.6 Hz and $^4J_{PH}$=3.0 Hz, 6*meta*CH), 7.55 (3H, dt, $^3J_{HH}$=7.6 Hz and $^5J_{PH}$=1.4 Hz, 3*para*CH), 7.67 (2H, d, J=8.7 Hz, 2CH), 7.67 (6H, dd, $^3J_{HH}$=7.6 Hz and $^3J_{PH}$=12.2 Hz, 6*ortho*CH). ^{13}C NMR: δ 25.98 (CH_3), 122.62 (d, $^3J_{PC}$=18.9 Hz, CH), 126.75 (C), 128.83 (d, $^3J_{PC}$=12.2 Hz, C^m), 129.98 (d, $^4J_{PC}$=1.6 Hz, CH), 130.01 (d, $^1J_{PC}$=99.8 Hz, C^{ipso}), 132.09 (d, $^4J_{PC}$=2.9 Hz, C^p), 132.56 (d, $^2J_{PC}$=9.7 Hz, C^o), 157.67 (d, $^2J_{PC}$=2.4 Hz, C–N=P), 196.63 (C=O). ^{31}P NMR: δ 6.53 (Ph_3P=N).

3.2.7. *N*-(2-Pyridyl)triphenyliminophosphorane 3g. Colorless crystals, mp 146–148°C (from ether), 0.35 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 1574, 1452, 1418, 1337, 1104, 1011. MS, *m*/*z* (%): 354 (M$^+$, 100), 277 (70), 199 (10), 183 (50), 152 (8), 94 (15), 77 (25). Anal. Calcd for $C_{23}H_{19}N_2P$ (354.39): C, 77.95; H, 5.40; N, 7.90. Found: C, 78.1; H, 5.4; N, 7.8%. ^{1}H NMR: δ 6.47 (1H, dd, J=7.0, 5.1 Hz, CH), 7.01 (1H, d, J=8.3 Hz, CH), 7.39 (1H, dt, $^3J_{HH}$=7.1 Hz and $^4J_{HH}$=1.1 Hz, CH), 7.43 (6H, dt, $^3J_{HH}$=7.6 and $^4J_{PH}$=3.0 Hz, 6*meta*CH), 7.50 (3H, dt, $^3J_{HH}$=7.6 Hz and $^5J_{PH}$=1.4 Hz, 3*para*CH), 7.86 (1H, d, $^3J_{HH}$=7.0 Hz, CH), 7.89 (6H, dd, $^3J_{HH}$=7.6 Hz and $^3J_{PH}$=12.2 Hz, 6*ortho*CH). ^{13}C NMR: δ 112.5 (CH), 117.16 (d, $^3J_{PC}$=24.0 Hz, CH), 128.83 (d, $^3J_{PC}$=12.0 Hz, C^m), 130.34

(d, $^1J_{PC}$=99.6 Hz, C^{ipso}), 131.36 (d, $^4J_{PC}$=2.6 Hz, C^p), 133.05 (d, $^2J_{PC}$=9.6 Hz, C^o), 136.50 (d, $^4J_{PC}$=4.5 Hz, CH), 146.95 (CH), 163.62 (d, $^2J_{PC}$=6.3 Hz, C–N=P). ^{31}P NMR: δ 14.25 (Ph_3P=N).

3.2.8. *N*-(5-Bromo-2-pyridyl)triphenyliminophosphorane 3h. Colorless crystals, mp 165–167°C (from 1:1 hexane–ethyl acetate), 0.42 g, yield 98%. IR (KBr) (ν_{max}/cm^{-1}): 1559, 1445, 1365, 1314, 1105, 1004. MS, *m*/*z* (%): 434 (M^++2, 95), 432 (M^+, 100), 277 (66), 199 (15), 183 (33), 152 (20), 78 (40). Anal. Calcd for $C_{23}H_{18}BrN_2P$ (433.29): C, 63.76; H, 4.19; N, 6.47. Found: C, 63.7; H, 4.2; N, 6.5%. ^{1}H NMR: δ 6.82 (1H, d, *J*=8.7 Hz, CH), 7.34 (1H, dd, $^3J_{HH}$=8.7 Hz and $^4J_{HH}$=2.1 Hz, CH), 7.38 (6H, td, $^3J_{HH}$=8.0 Hz and $^4J_{PH}$=2.3 Hz, 6*meta*CH), 7.44 (3H, t, $^3J_{HH}$=7.5 Hz, 3*para*CH), 7.78 (6H, dd, $^3J_{HH}$=8.0 Hz and $^3J_{PH}$=12.0 Hz, 6*ortho*CH), 7.80 (1H, d, $^4J_{HH}$=2.1 Hz, CH). ^{13}C NMR: δ 107.24 (C–Br), 118.99 (d, $^3J_{PC}$=24.0 Hz, CH), 128.28 (d, $^3J_{PC}$=12.0 Hz, C^m), 129.81 (d, $^1J_{PC}$=99.9 Hz, C^{ipso}), 131.55 (d, $^4J_{PC}$=2.6 Hz, C^p), 133.02 (d, $^2J_{PC}$=9.7 Hz, C^o), 138.91 (d, $^4J_{PC}$=4.5 Hz, CH), 147.43 (CH), 162.44 (d, $^2J_{PC}$=6.5 Hz, C–N=P). ^{31}P NMR: δ 14.62 (Ph_3P=N).

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