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Lotfali Saghatforoush[a]; Malek T. Maghsoodlou[b]; Ali Aminkhani[a]; Ghasem Marandi[b]; Roya Kabiri[c]
[a] Faculty of Science, Payame Nour University of Khoy, Khoy, Iran [b] Department of Chemistry, The University of Sistan and Balouchestan, Zahedan, Iran [c] Faculty of Chemistry, The University of Tarbriz, Tabriz, Iran

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RESEARCH ARTICLE

One-pot synthesis of stable phosphonium ylides using 2-mercaptopyrimidine derivatives

LOTFALI SAGHATFOROUSH†, MALEK T. MAGHSOODLOU*‡, ALI AMINKHANI†, GHASEM MARANDI‡ and ROYA KABIRI§

†Faculty of Science, Payame Nour University of Khoy, Khoy, Iran
‡Department of Chemistry, The University of Sistan and Balouchestan, PO Box 98135-674, Zahedan, Iran
§Faculty of Chemistry, The University of Tarbriz, Tabriz, Iran

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The reaction of dialkyl acetylenedicarboxylates with 2-mercaptopyrimidine and 2-mercapto-4,6-dimethylpyrimidine in the presence of triphenylphosphine leads to stable phosphorus ylides in excellent yields. These stable ylides exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon-carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbon group.

Keywords: Acetylenic esters; Stable phosphorus ylides; Triphenylphosphine; 2-mercaptopyrimidine; 2-mercapto-4,6-dimethylpyrimidine; Geometrical isomers

1. Introduction

The development of simple synthesis routes for widely used organic compounds from readily available reagents is one of the most important tasks in organic chemistry [1]. Pyrimidine derivatives have been employed in a wide range of medicinal chemistry because of their diverse biological activities, such as antibacterial [2, 3], anticonvulsant [4], antiflammatory [5–7], antitumor [8–10] and antifungal activities [11]. In addition, phosphorus ylides from pyrimidine derivatives are important reagents in synthetic organic chemistry, especially in the synthesis of naturally occurring products, compound with biological and pharmacological activity [12]. These ylides are most often prepared by treatment of a phosphonium salt with a base. The phosphonium salts are usually made from the phosphine and an alkyl halide [13–17] but they are also obtained by Michael addition of phosphorus nucleophiles to activated olefins [13, 14]. In the current work, we wish to describe an efficient synthetic route of the 2-mercaptopyrimidine and also 2-mercapto-4,6-dimethylpyrimidine-containing phosphorus ylides [18–21]. With respect to the importance of the mentioned purpose the present work was undertaken for the generation

*Corresponding author. Email: MT_maghsoodlou@yahoo.com

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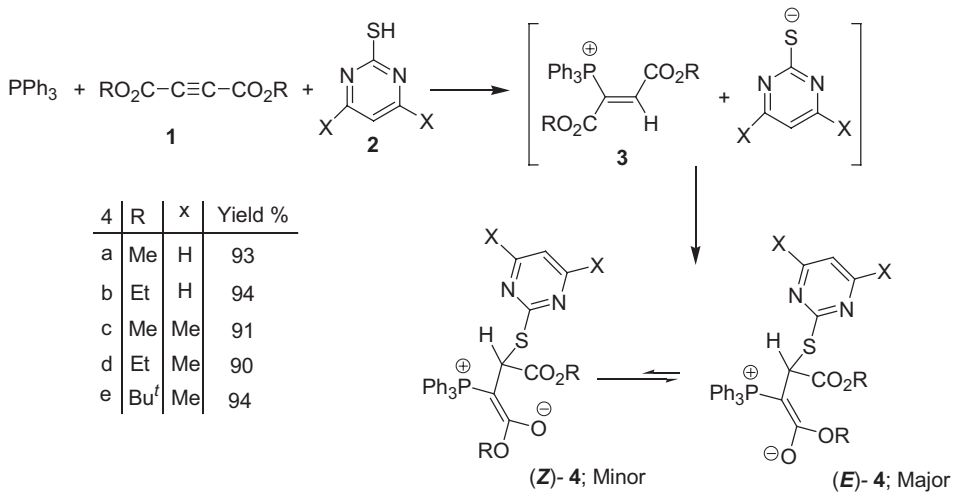

4	R	X	Yield %
a	Me	H	93
b	Et	H	94
c	Me	Me	91
d	Et	Me	90
e	Bu^t	Me	94

SCHEME 1

of stable sulfur-containing phosphoranes. In order to do this, the reaction of triphenylphosphine with dialkyl acetylenedicarboxylates (**1**) in the presence of strong SH-acids (**2**) led to the vinyltriphenylphosphonium cation (**3**), which was subsequently followed by attack of the 2-mercaptopyrimidine or 2-mercapto-4,6-dimethylpyrimidine anion to form the phosphoranes (***4-E***) and (***4-Z***) in excellent yields (see scheme 1).

2. Results and discussion

The reaction of 2-mercaptopyrimidine or 2-mercapto-4,6-dimethylpyrimidine (**2**) with dialkyl acetylenedicarboxylates (**1**) in the presence of triphenylphosphine was conducted in ethyl acetate solvent at room temperature and was complete within a few hours. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides (**4**). No other product could be detected by NMR spectroscopy. The structures of compound **4a–e** were deduced from their IR, ^{1}H, ^{13}C, ^{31}P NMR and mass spectroscopic data. The mass spectra of them displayed molecular ion peak at appropriate m/z values. Any fragmentations involve partial 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 **4a–e** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation around the partial double bond in (***Z***)-**4** and (***E***)-**4** geometrical isomers (see scheme 1) is slow on the NMR timescale at ambient temperature.

Selected ^{1}H, ^{13}C and ^{31}P NMR chemical shifts and coupling constant in the major and minor geometrical isomers of compound (**4**) are shown in the experimental section. On the basis of the well established chemistry of trivalent phosphorus nucleophiles, [13–17] it is reasonable to assume that phosphorus ylide (**4**) results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the S-H acid to form phosphorus ylide (**4**).

In summary, we have prepared novel 2-mercaptopyrimidine and 2-mercapto-4,6-dimethylpyrimidine-containing phosphorus ylides via one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong S-H acids such

as 2-mercapto-4,6-dimethylpyrimidine or 2-mercaptopyrimidine. The present method carries the advantage that, not only is the reaction performed under the neutral conditions, but also the substances can be mixed without any activation or modifications [22–30]. It should be noticed that, 2-mercaptopyrimidine and 2-mercapto-4,6-dimethylpyrimidine-containing phosphorus ylides **4a**–**e** 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.

3. Experimental

Melting points and IR spectra of all compounds were measured on an Electrothermal 9100 apparatus and a Shimadzu IR-460 spectrometer, respectively. Elemental analysis for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained from a Bruker DRX-400 Avance instrument with $CDCl_3$ as solvent at 400.1, 100.6, and 161.9 MHz, respectively. Mass spectra were recorded on a HP (Agilent Technology) GC/MS MSD (5973) mass spectrometer operating at an ionization potential of 70 eV. Triphenylphosphine, dialkyl acetylenedicarboxylates, 2-mercaptopyrimidine and 2-mercapto-4,6-dimethylpyrimidine were purchased from Fluka (Buchs, Switzerland) and used without further purification.

3.1 *Preparation of dimethyl 2-(pyrimidine-2-sulfanyl)-3-(triphenyl phosphanylidene) butanedioate (4a)*

3.1.1 General procedure. To a magnetically stirred solution of 2-mercaptopyrimidine (0.11 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in 8 mL of ethyl acetate was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.14 g, 1 mmol) in 4 mL of ethyl acetate at −5 °C over 10 min. After approximately 10 hours of stirring at room temperature, the product was filtered and washed with cold diethyl ether (2 × 3 mL) and extracted as pale white powder (0.48 g, 93%), mp 168–171 °C; IR (υ_{max}, cm^{-1}) 1735, 1607 (C=O); MS (*m*/*z*, %) 516 (M, 2), 485 (2), 405 (100), 262 (90), 108 (21). Anal. Calc. for $C_{28}H_{25}N_2O_4PS$ (516): C, 65.12; H, 4.84; N, 5.43%; Found: C, 64.97; H, 4.91; N, 5.57%.

Major isomer (*E*)-**4a** (65%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ_H 3.59 and 3.69 (6H, 2s, 2 CO_2Me), 4.86 (1H, d, $^{3}J_{PH}$ 19.2 Hz, P−C−C*H*), 6.71 (1H, t, J = 7.2 Hz, Ar−H), 7.40–7.74 (15H, m, 3 C_6H_5), 8.17 (2H, d, J = 7.2 Hz, Ar−H). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ_C 40.51 (d, $^{1}J_{PC}$ 137.4 Hz, P=C), 49.02 (d, $^{2}J_{PC}$ 15.2 Hz, P−C−*C*H), 48.94 and 49.21 (2s, 2 OCH_3), 114.29 (CH_{arom}), 124.87 (d, $^{1}J_{PC}$ 92.3 Hz, C_{ipso}), 127.59 (d, $^{3}J_{PC}$ 11.9 Hz, C_{meta}), 130.84 (d, $^{4}J_{PC}$ 1.8 Hz, C_{para}), 132.63 (d, $^{2}J_{PC}$ 9.7 Hz, C_{ortho}), 155.45 (s, 2 N*C*H$_{arom}$), 169.38 (d, $^{3}J_{PC}$ 18.2 Hz, C=O), 171.84 (d, $^{2}J_{PC}$ 13.9 Hz, P−C=*C*), 172.23 (NCN). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ_P 23.90 (Ph_3P^+−C).

Minor isomer (*Z*)-**4a** (35%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ_H 3.69 and 3.80 (6H, 2s, 2 CO_2Me), 4.93 (1H, d, $^{3}J_{PH}$ 18.1 Hz, P−C−C*H*), 6.73 (1H, t, J = 4.2 Hz, Ar−H), 7.40–7.74 (15H, m, 3 C_6H_5), 8.18 (2H, d, J = 4.2 Hz, Ar−H). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ_C 39.84 (d, $^{1}J_{PC}$ 128.6 Hz, P=C), 49.65 (d, $^{2}J_{PC}$ 15.5 Hz, P−C−*C*H), 51.22 and 51.58 (2s, 2 OCH_3), 114.40 (CH_{arom}), 125.53 (d, $^{1}J_{PC}$ 92.1 Hz, C_{ipso}), 127.48 (d, $^{3}J_{PC}$ 9.36 Hz, C_{meta}), 130.86 (d, $^{4}J_{PC}$ 2.0 Hz, C_{para}), 132.45 (d, $^{2}J_{PC}$ 9.5 Hz, C_{ortho}), 156.28 (2 N*C*H$_{arom}$), 168.96 (d, $^{3}J_{PC}$ 13.0 Hz, C=O), 171.76 (d, $^{2}J_{PC}$ 14.1 Hz, P−C=*C*), 172.00 (NCN). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ_P 23.37 (Ph_3P^+−C).

3.2 *Diethyl 2-(pyrimidine-2-sulfanyl)-3-(triphenyl phosphanylidene) butanedioate (4b)*

Pale white powder (0.51 g, 94%), mp 130–133 °C; IR (υ_{max}, cm^{-1}) 1730, 1602 (C=O); MS (*m/z*, %) 544 (M, 1), 499 (3), 471 (4), 433 (100), 262 (97), 108 (25). Anal. Calc. for $C_{30}H_{29}N_2O_4PS$ (544): C, 66.17; H, 5.33; N, 5.15%; Found: C, 66.25; H, 5.41; N, 5.06%.

Major isomer (*E*)-**4b** (59%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ_H 0.43 and 1.20 (6H, 2t, $J = 7.0$ Hz, 2 $CO_2CH_2CH_3$), 3.71 and 4.09 (4H, 2 m, ABX_3 system, 2 $CO_2CH_2CH_3$), 4.84 (1H, d, $^3J_{PH}$ 19.2 Hz, P−C−C*H*), 6.70 (1H, t, $J = 4.5$ Hz, Ar−H), 7.41–7.54 (15H, m, 3 C_6H_5), 8.18 (2H, $J = 4.5$ Hz, Ar−H). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ_C 12.86 and 13.11 (2 OCH_2CH_3), 40.72 (d, $^1J_{PC}$ 138.1 Hz, P=C), 49.30 (d, $^2J_{PC}$ 15.0 Hz, P−C−*C*H), 56.67 and 60.25 (2s, 2 OCH_2CH_3), 114.23 (CH_{arom}), 125.11 (d, $^1J_{PC}$ 91.8 Hz, C_{ipso}), 127.42 (d, $^3J_{PC}$ 12.8 Hz, C_{meta}), 130.79 (C_{para}), 132.69 (d, $^2J_{PC}$ 9.1 Hz, C_{ortho}), 155.40 (2 N*C*H_{arom}), 171.14 (d, $^3J_{PC}$ 19.7 Hz, C=O), 171.33 (NCN), 172.33 (d, $^2J_{PC}$ 20.6 Hz, P−C=*C*). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ_P 23.26 (Ph_3P^+−C).

Minor isomer (*Z*)-**4b** (41%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ_H 1.25 and 1.27 (6H, 2t, $J = 7.1$ Hz, 2 $CO_2CH_2CH_3$), 4.04 and 4.19 (4H, 2 m, ABX_3 system, 2 $CO_2CH_2CH_3$), 4.94 (1H, d, $^3J_{PH}$ 18.6 Hz, P−C−C*H*), 6.72 (1H, t, $J = 4.5$ Hz, Ar−H), 7.67–7.74 (15H, m, 3 C_6H_5), 8.18 (2H, $J = 4.5$ Hz, Ar−H). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ_C 13.11 and 13.85 (2 OCH_2CH_3), 39.59 (d, $^1J_{PC}$ 131.0 Hz, P=C), 49.89 (d, $^2J_{PC}$ 15.6 Hz, P−C−*C*H), 57.30 and 60.25 (2s, 2 OCH_2CH_3), 114.31 (CH_{arom}), 125.77 (d, $^1J_{PC}$ 91.9 Hz, C_{ipso}), 127.54 (d, $^3J_{PC}$ 12.9 Hz, C_{meta}), 131.02 (C_{para}), 132.71 (d, $^2J_{PC}$ 9.1 Hz, C_{ortho}), 155.40 (2 N*C*H_{arom}), 167.98 (d, $^3J_{PC}$ 12.3 Hz, C=O), 169.04 (d, $^2J_{PC}$ 12.6 Hz, P−C=*C*), 171.42 (NCN). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ_P 23.69 (Ph_3P^+−C).

3.3 *Dimethyl 2-(4,6-dimethylpyrimidine-2-sulfanyl)-3-(triphenyl phosphanylidene) butanedioate (4c)*

Pale white powder (0.49 g, 91%), mp 189–192 °C; IR (υ_{max}, cm^{-1}) 1743, 1611 (C=O); MS (*m/z*, %) 544 (M, 3), 513 (2), 485 (5), 405 (100), 262 (91), 108 (17). Anal. Calc. for $C_{30}H_{29}N_2O_4PS$ (544): C, 66.17; H, 5.33; N, 5.15%; Found: C, 65.87; H, 5.41; N, 5.29%.

Major isomer (*E*)-**4c** (59%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ_H 2.15 (6H, s, Ar*Me*$_2$), 3.76 and 3.81 (6H, 2s, 2 CO_2Me), 4.88 (1H, d, $^3J_{PH}$ 19.7 Hz, P−C−C*H*), 6.68 (1H, s, Ar−H), 7.31–7.75 (15H, m, 3 C_6H_5). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ_C 22.41 (s, Ar*Me*$_2$), 40.19 (d, $^1J_{PC}$ 137.2 Hz, P=C), 48.44 (d, $^2J_{PC}$ 15.3 Hz, P−C−*C*H), 49.35 and 51.28 (2s, 2 OCH_3), 113.45(CH_{arom}), 124.77 (d, $^1J_{PC}$ 92.2 Hz, C_{ipso}), 127.38 (d, $^3J_{PC}$ 12.0 Hz, C_{meta}), 130.61 (d, $^4J_{PC}$ 2.3 Hz, C_{para}), 132.49 (d, $^2J_{PC}$ 9.9 Hz, C_{ortho}), 164.84 (s, 2 *C*Me), 169.31 (d, $^3J_{PC}$ 18.5 Hz, C=O), 170.36 (NCN), 171.93 (d, $^2J_{PC}$ 10.7 Hz, P−C=*C*). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ_P 23.86 (Ph_3P^+−C).

Minor isomer (*Z*)-**4c** (41%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ_H 2.31 (6H, s, Ar*Me*$_2$), 3.67 and 3.74 (6H, 2s, 2 CO_2Me), 4.96 (1H, d, $^3J_{PH}$ 18.9 Hz, P−C−C*H*), 6.75 (1H, s, Ar−H), 7.31–7.75 (15H, m, 3 C_6H_5). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ_C 22.41 (s, Ar*Me*$_2$), 33.32 (d, $^1J_{PC}$ 128.8 Hz, P=C), 49.27 (d, $^2J_{PC}$ 15.4 Hz, P−C−*C*H), 47.89 and 51.28 (2s, 2 OCH_3), 113.31 (CH_{arom}), 125.44 (d, $^1J_{PC}$ 91.9 Hz, C_{ipso}), 127.27 (d, $^3J_{PC}$ 10.8 Hz, C_{meta}), 130.70 (d, $^4J_{PC}$ 2.4 Hz, C_{para}), 132.49 (d, $^2J_{PC}$ 9.9 Hz, C_{ortho}), 164.77 (s, 2 *C*Me), 168.14 (d, $^3J_{PC}$ 13.58 Hz, C=O), 170.69 (NCN), 171.79 (d, $^2J_{PC}$ 10.5 Hz, P−C=*C*). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ_P23.56 (Ph_3P^+−C).

3.4 *Diethyl 2-(4,6-dimethylpyrimidine-2-sulfanyl)-3-(triphenyl phosphanylidene) butanedioate (4d)*

White powder (0.51 g, 90%), mp 147–150 °C; IR (υ_{max}, cm^{-1}) 1738, 1629 (C=O); MS (*m/z*, %) 572 (M, 1), 499 (3), 433 (77), 262 (100), 108 (22). Anal. Calc. for $C_{32}H_{33}N_2O_4PS$ (572): C, 67.13; H, 5.77; N, 4.90%; Found: C, 67.28; H, 5.67; N, 5.02%.

Major isomer (*E*)-**4d** (55%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ 0.38 (3H, t, $J = 6.1$ Hz, $CO_2CH_2CH_3$), 1.13 (3H, t, $J = 6.8$ Hz, $CO_2CH_2CH_3$), 2.11 (6H, s, ArMe_2), 3.67 and 4.01 (4H, 2 m, 2 ABX_3 system, 2 OCH_2CH_3), 4.82 (1H, d, $^3J_{PH}$ 19.6 Hz, P−C−C*H*), 6.43 (1H, s, Ar−H), 7.37–7.73 (15H, m, 3 C_6H_5). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 12.93 and 13.11 (2 OCH_2CH_3), 22.60 (s, ArMe_2), 40.30 (d, $^1J_{PC}$ 137.9 Hz, P=C), 47.67 (d, $^2J_{PC}$ 15.1 Hz, P−C−*C*H), 57.20 and 60.73 (2s, 2 OCH_2CH_3), 113.75 (CH_{arom}), 124.91 (d, $^1J_{PC}$ 91.7 Hz, C_{ipso}), 127.39 (d, $^3J_{PC}$ 10.6 Hz, C_{meta}), 130.83 (d, $^4J_{PC}$ 2.7 Hz, C_{para}), 131.56 (d, $^2J_{PC}$ 9.9 Hz, C_{ortho}), 165.94 (s, 2 *C*Me), 168.82 (d, $^3J_{PC}$ 19.3 Hz, C=O), 170.54 (NCN), 169.95 (d, $^2J_{PC}$ 11.5 Hz, P−C=*C*). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ 23.87 (Ph_3P^+−C).

Minor isomer (*Z*)-**4d** (45%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ 1.18–1.28 (6H, m, 2 $CO_2CH_2CH_3$), 2.11 (6H, s, ArMe_2), 4.07 and 4.16 (4H, 2 m, 2 ABX_3 system, 2 OCH_2CH_3), 4.93 (1H, d, $^3J_{PH}$ 19.1 Hz, P−C−C*H*), 6.43 (1H, s, Ar−H), 7.33–7.73 (15H, m, 3 C_6H_5). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 13.63 and 13.74 (2 OCH_2CH_3), 22.60 (s, ArMe_2), 37.58 (d, $^1J_{PC}$ 128.4 Hz, P=C), 48.57 (d, $^2J_{PC}$ 15.6 Hz, P−C−*C*H), 56.86 and 60.73 (2s, 2 OCH_2CH_3), 114.87 (CH_{arom}), 125.56 (d, $^1J_{PC}$ 91.9 Hz, C_{ipso}), 127.15 (d, $^3J_{PC}$ 11.3 Hz, C_{meta}), 130.89 (d, $^4J_{PC}$ 2.3 Hz, C_{para}), 131.11 (d, $^2J_{PC}$ 9.9 Hz, C_{ortho}), 165.91 (s, 2 *C*Me), 168.30 (d, $^3J_{PC}$ 12.9 Hz, C=O), 170.43 (NCN), 170.91 (d, $^2J_{PC}$ 10.5 Hz, P−C=*C*). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ 23.56 (Ph_3P^+−C).

3.5 *Di tert-butyl 2-(4,6-dimethylpyrimidine-2-sulfanyl)-3-(triphenyl phosphanylidene) butanedioate (4e)*

Pale white powder (0.60 g, 94%), mp 145–148 °C; IR (υ_{max}, cm^{-1}) 1727, 1627 (C=O); MS (*m/z*, %) 628 (M, 1), 555 (1), 527 (3), 489 (39), 262 (100), 108 (21), 57 (35). Anal. Calc. for $C_{36}H_{41}N_2O_4PS$ (628): C, 68.79; H, 6.53; N, 4.46%; Found: C, 68.82; H, 6.61; N, 4.50%.

Major isomer (*E*)-**4e** (56%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ 1.42 and 1.48 (18H, 2s, 2 CO_2CMe_3), 2.11 (6H, s, ArMe_2), 4.55 (1H, d, $^3J_{PH}$ 20.1 Hz, P−C−C*H*), 6.39 (1H, s, Ar−H), 7.36–7.52 (15H, m, 3 C_6H_5). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 22.51 (s, ArMe_2), 27.08 and 27.73 (2s, 2 CMe_3), 38.94 (d, $^1J_{PC}$ 129.8 Hz, P=C), 49.96 (d, $^2J_{PC}$ 15.9 Hz, P−C−*C*H), 78.63 and 78.78 (2s, 2 O*C*Me$_3$), 113.09 (CH_{arom}), 125.73 (d, $^1J_{PC}$ 91.8 Hz, C_{ipso}), 127.42 (d, $^3J_{PC}$ 11.9 Hz, C_{meta}), 130.50 (C_{para}), 132.73 (d, $^2J_{PC}$ 9.8 Hz, C_{ortho}), 164.74 (s, 2 *C*Me), 169.38 (d, $^3J_{PC}$ 16.2 Hz, C=O), 170.23 (d, $^2J_{PC}$ 10.5 Hz, P−C=*C*), 171.54 (NCN). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ 22.97 (Ph_3P^+−C).

Minor isomer (*Z*)-**4e** (44%): ^{1}H NMR (400.1 MHz; $CDCl_3$) δ 1.43 and 1.49 (18H, 2s, 2 CO_2CMe_3), 2.39 (6H, s, ArMe_2), 4.77 (1H, d, $^3J_{PH}$ 19.0 Hz, P−C−C*H*), 6.45 (1H, s, Ar−H), 7.63–7.76 (15H, m, 3 C_6H_5). ^{13}C NMR (100.6 MHz; $CDCl_3$) δ 22.51 (s, ArMe_2), 26.09 and 27.28 (2s, 2 CMe_3), 41.16 (d, $^1J_{PC}$ 136.8 Hz, P=C), 51.17 (d, $^2J_{PC}$ 15.8 Hz, P−C−*C*H), 80.59 and 80.64 (2s, 2 O*C*Me$_3$), 109.91 (CH_{arom}), 126.49 (d, $^1J_{PC}$ 92.1 Hz, C_{ipso}), 127.17 (d, $^3J_{PC}$ 12.7 Hz, C_{meta}), 130.87 (d, $^4J_{PC}$ 2.4 Hz, C_{para}), 132.87 (d, $^2J_{PC}$ 9.9 Hz, C_{ortho}), 164.67 (s, 2 *C*Me), 167.41 (d, $^3J_{PC}$ 13.6 Hz, C=O), 169.53 (d, $^2J_{PC}$ 10.1 Hz, P−C=*C*), 172.35 (NCN). ^{31}P NMR (161.9 MHz; $CDCl_3$) δ 23.94 (Ph_3P^+−C).

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