
**Journal of Sulfur Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

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**To cite this Article** Aminkhani, Ali , Kabiri, Roya , Habibi-Khorassani, Sayyed Mostafa , Heydari, Reza , Maghsoodlou, Malek Taher , Marandi, Ghasem , Lashkari, Mojtaba and Rostamizadeh, Mohsen(2009) 'Synthesis of heterocyclic phosphonato esters by reaction between triphenyl phosphite and acetylenic diesters in the presence of sulfur-containing heterocyclic compounds', Journal of Sulfur Chemistry, 30: 5, 500 — 506
**To link to this Article: DOI:** 10.1080/17415990902839450
**URL:** http://dx.doi.org/10.1080/17415990902839450

*Journal of Sulfur Chemistry*
Vol. 30, No. 5, October 2009, 500–506

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# Synthesis of heterocyclic phosphonato esters by reaction between triphenyl phosphite and acetylenic diesters in the presence of sulfur-containing heterocyclic compounds

Ali Aminkhani[a]*, Roya Kabiri[b], Sayyed Mostafa Habibi-Khorassani[c], Reza Heydari[c], Malek Taher Maghsoodlou[c]*, Ghasem Marandi[c], Mojtaba Lashkari[c] and Mohsen Rostamizadeh[c]

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(*Received 24 January 2009; final version received 17 February 2009*)



The reaction between triphenyl phosphite and acetylenic esters in the presence of some heterocyclic compounds such as oxazolo[4,5-*b*]pyridine-2(3*H*)-thione, 2-mercaptobenzothiazole or 2-mercaptopyrimidine led to the formation of phosphonato esters in high yield.

**Keywords:** triphenyl phosphite; acetylenic esters; phosphonato esters; Karplus equation; diastereoisomers

## 1. Introduction

Heterocyclic systems with oxygen, nitrogen, sulfur and other heteroatoms in five and six-membered rings, and also phosphorus compounds are of interest because of the pharmaceutical and biological activities such as anti-inflammatory, cardiotonic, inotropic, antihypertensive, antimicrobial and antibacterial (*1*, *2*). Numerous studies have been reported previously using the reaction between trivalent phosphorus nucleophiles and deficient carbonyl compounds in the presence of a proton source, such as CH, NH, OH or SH compounds (*3*).

In the set of investigations made on the development of organophosphorus heterocyclic compound synthesis (3*g*–*l*, *4*), we now describe a one-pot, synthesis of heterocyclic phosphonato ester derivatives **3** and **5** using triphenyl phosphite and acetylenic diesters **1** in the presence of protic heterocyclic compounds **2** or **4**.

## 2. Results and discussion

The works undertaken were to carry out synthesis of the reactions between triphenyl phosphite, acetylenic esters **1** in the presence of protic heterocyclic compounds (**2** or **4**) in appropriate

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ISSN 1741-5993 print/ISSN 1741-6000 online

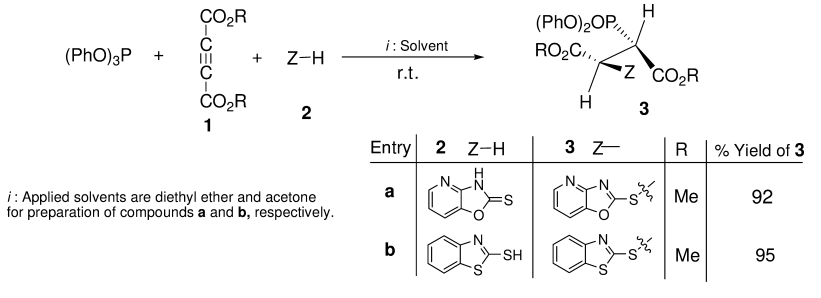
DOI: 10.1080/17415990902839450
http://www.informaworld.com

solvent. These reactions proceeded smoothly at room temperature and were completed within 3–15 h in high yield. TLC and $^1$H NMR spectra of the crude products clearly indicated formation of phosphonate esters **3** or **5** (see Schemes 1, 2 and 5).

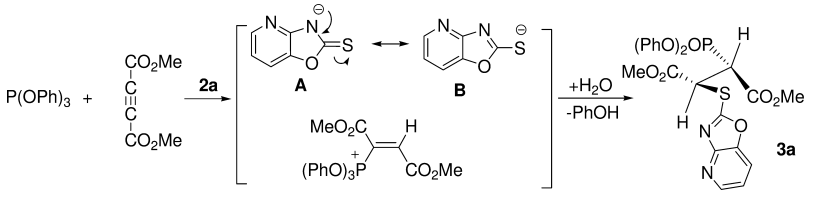
The essential structures of the products **3a** and **3b** or **5a** and **5b** were deduced from elemental analysis, IR, $^1$H, $^{13}$C, $^{31}$P NMR and mass spectra. The mass spectra of these compounds displayed molecular ion peaks at appropriate $m/z$ values, any initial fragmentation involves the loss of the ester and phenoxy moieties. No product other than **3a** and **3b** or **5a** and **5b** could be detected by NMR spectroscopy.

The $^1$H NMR spectra of **3a** and **3b** showed two singlets at ($\delta = 3.73$, 3.91 ppm) and ($\delta = 3.73$, 3.87 ppm) for methoxy protons and also exhibited a multiplet at ($\delta = 6.76$–8.13 ppm) and ($\delta = 7.02$–7.57 ppm) for aromatic protons of each compound. In addition, two doublet of doublets were observed for the vicinal methine protons of each compound ($\delta = 5.19$, $^3J_{HH} = 11.6$, $^2J_{HP} = 20.7$ Hz and $\delta = 6.56$, $^3J_{HH} = 11.6$, $^3J_{HP} = 5.3$ Hz) and ($\delta = 5.64$, $^3J_{HH} = 11.1$, $^2J_{HP} = 20.8$ Hz and $\delta = 6.03$, $^3J_{HH} = 11.1$, $^3J_{HP} = 5.5$ Hz), respectively. The vicinal proton–proton coupling constant ($^3J_{HH}$) can be obtained from the Karplus equation as a function of the torsion angle (*5*). Typically $J_{gauche}$ and $J_{anti}$ configurations give rise to distinct coupling constant, which vary between 1.5 and 10–14, respectively (*5*). Observation of $^3J_{HH} = 11.6$ and 11.1 Hz for the vicinal protons in compound **3a** and **3b**, respectively, confirm an *anti*-arrangement for these protons. Since compounds **3a** and **3b** possess two stereogenic centers, two diastereoisomers [(2S, 3R)-**3a** or (2R, 3S)-**3a** and (2S, 3S)-**3a** or (2R, 3R)-**3a**] with anti HCCH arrangement are possible (Scheme 3).

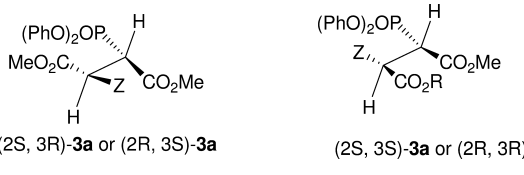





Scheme 1.




Scheme 2.



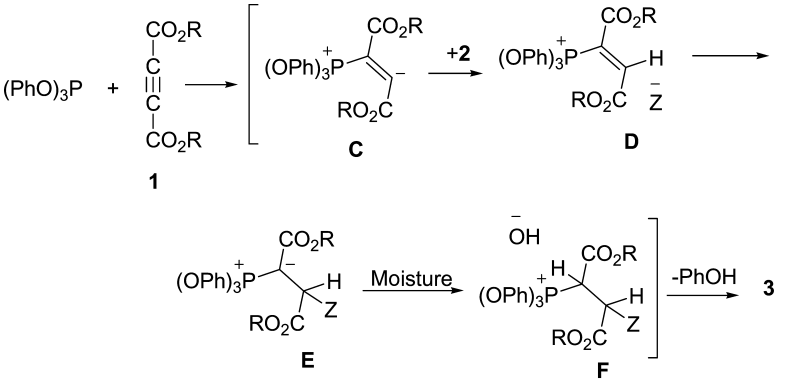

Scheme 3.

The presence of phosphorus ($^{31}$P) nucleus in the compounds **3a** and **3b** assist in identifying its configuration by analyzing the long-range spin–spin coupling signals of phosphorus ($^{31}$P) nucleus with neighboring protons ($^{1}$H) and carbon ($^{13}$C) nuclei (see Experimental).

The carbon–phosphorus three bond range coupling constant $^{3}J_{CP}$ is associated with the *anti* or *cis* configuration (transoid coupling being larger than cisoid coupling, (*5d*). The Karplus relationship can be derived from the literature data for organophosphorus compounds with tetra- or penta-valant phosphorus environments (*5a*). The observation of $^{3}J_{CP} = 19.4$ and 18.7 Hz at $\delta = 165.9$ and $\delta = 167.4$ ppm for the distal ester carbonyl group of compounds **3a** and **3b**, respectively, are in agreement with an *anti*-arrangement along the P–CH–CH–CO bond. These assignments were reinforced in each compounds (**3a** and **3b**) with the smaller coupling of the phosphorus to the proximal ester carbon group, $^{2}J_{CP} = 7.4$ and 8.1 Hz at $\delta = 165.2$ and $\delta = 164.8$ ppm, respectively.

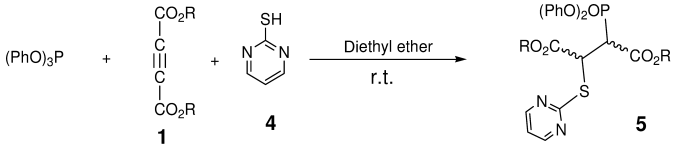
On the basis of the proposed mechanism in the literature (*6*, *7*), it is reasonable to assume that the heterocyclic phosphonato ester **3** results from the initial addition of triphenyl phosphite to the acetylenic ester **1** (1:1 adduct or zwitterionic **C**), and subsequent protonation of the 1:1 adduct by the protic heterocyclic compound **2** to generate intermediate of phosphonium ion **D**, which was followed by the conjugate base ($\mathbf{Z}^-$) to produce ylide **E**. It is converted to **F** in the presence of moisture and subsequent loss of PhOH (see Scheme 4).






Scheme 4.

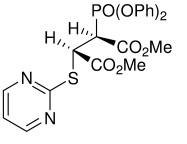
The $^{1}$H NMR spectra of **5a** showed four singlets at ($\delta = 3.73$, 3.78 ppm) and ($\delta = 3.71$, 3.81 ppm) for methoxy protons in agreement with two diastereoisomers (major and minor) of



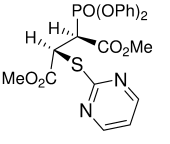

| 5 | Z | R | % Yield of **5**, Major and minor | | |
|---|---|---|---|---|---|
| **a** |  | Me | 96 | 58 | 42 |
| **b** | | Et | 93 | 61 | 39 |

Scheme 5.

phosphonato esters **5a,** respectively, and also exhibited a multiplet at ($\delta = 6.98$–$8.53$ ppm) and ($\delta = 7.00$–$8.58$ ppm) for aromatic protons of each diastereoisomer. The $^1$H NMR spectra of **5a** display two doublets of doublets for the vicinal methine protons of each isomer (major and minor) ($\delta = 4.35$, $^3J_{HH} = 6.6$, $^2J_{HP} = 24.6$ Hz and $\delta = 5.81$, $^3J_{HH} = 6.6$, $^3J_{HP} = 9.5$ Hz) and ($\delta = 4.42$, $^3J_{HH} = 7.9$, $^2J_{HP} = 24.4$ Hz and $\delta = 5.45$, $^3J_{HH} = 7.9$, $^3J_{HP} = 9.5$ Hz), respectively. The vicinal proton–proton coupling constant ($^3J_{HH}$) can be obtained from the Karplus equation as a function of the torsion angle (5). Observation of $^3J_{HH} = 6.6$ and 7.9 Hz for the vicinal protons in two diastereoisomers of **5a** (major and minor), respectively, confirms a *gauche*-arrangement for these protons. Since compounds **5a** (major and minor) possess two stereogenic centers, two diastereoisomers [(2S, 3S)-**5a** or (2R, 3R)-**5a** and (2S, 3R)-**5a** or (2R, 3S)-**5a**] with *gauche* HCCH arrangement are possible (Scheme 6). Any attempts for separation of major- and minor-**5a** were unsuccessful.




(2S, 3S)-**5a** or (2R, 3R)-**5a**




(2S, 3R)-**5a** or (2R, 3S)-**5a**

Scheme 6.

In conclusion, the reaction between triphenyl phosphite and acetylenic esters in the presence of NH or SH-acids such as oxazolo[4,5-*b*]pyridine-2(3*H*)-thione, 2-mercaptobenzothiazole or 2-mercaptopyrimidine provides a simple one-pot entry into the synthesis of stable phophonato esters of potential interest. The present procedure has the advantage that not only is the reaction performed under neutral conditions, but also the substances can be mixed without any activation or modifications.



## 3. Experimental

Melting points and IR spectra were taken on an Electrothermal 9100 apparatus and a JASCO FT-IR spectrometer, respectively. The $^1$H, $^{13}$C and $^{31}$P NMR spectra were recorded on a Bruker DRX-400 AVANCE instrument with $CDCl_3$ as solvent at 400.1, 100.6 and 161.9 MHz, respectively. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyzer. The mass spectra were recorded on a Shimadzu GCMS-QP5050A mass spectrometer operating at an ionization potential of 70 eV. Triphenyl phosphite, dialkyl acetylendicarboxylate, oxazolo [4,5-*b*]pyridine-2(3*H*)-thione, 2-mercaptobenzothiazole and 2-mercaptopyrimidine purchased from Merck, Fluka and Acros, and used without further purifications.

*General procedure (Exemplified by **3a**)*

To a stirred solution of oxazolo[4,5-*b*]pyridine-2(3*H*)-thione (1 mmol) and dimethyl acetylendicarboxylate (1 mmol) in 10 mL diethyl ether was added, drop wise, a mixture of triphenyl phosphite (1 mmol) in 5 mL diethyl ether at $-5$ °C over 10 min. The mixture was then allowed to warm up to room temperature and stirred for 5 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography ($SiO_2$; *n*-hexane/EtOAc = 3/1) to afford the pure adducts.

*Dimethyl 2-[bis(phenyloxy)-phosphoryl]-3-(oxazolo[4,5-b]pyridine-2-thio-S-yl)butandioate (**3a**)*

Pale white powder: yield (0.49 g), mp 87–90 °C, IR (KBr) ($\upsilon_{max}$, $cm^{-1}$): 1738 and 1744 (C = O). MS ($m/z$, %): 528 ($M^+$, 7), 435 (10), 376 (26), 345 (14), 317 (33), 285 (95), 152 (100), 93 (18), 59 (10). Anal. Calcd for $C_{24}H_{21}N_2O_8PS$ (528.47): C, 54.55; H, 4.01; N, 5.30. Found: C, 54.48; H, 4.02; N, 5.37.

$^1$H NMR (400.1 MHz, $CDCl_3$): $\delta_H$ 3.73 and 3.91 (6H, 2s, 2 OMe), 5.19 (1H, dd, $^2J_{HP}$ = 20.7 and $^3J_{HH}$ = 11.6 Hz, P–C*H*–CH), 6.56 (1H, dd, $^3J_{HH}$ = 11.6 and $^3J_{HP}$ = 5.3 Hz, P–CH–C*H*), 6.76 (1H, d, $^3J_{HH}$ = 7.9 Hz, $CH_{Het}$), 6.87 (1H, uneven t, $^3J_{HH}$ = 7.3 Hz, $CH_{Het}$), 6.94–7.35 (10H, m, 2 OPh), 8.13 (1H, d, $^3J_{HH}$ = 4.9 Hz, $CH_{Het}$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta_C$ 42.22 (d, $^1J_{PC}$ = 135.8 Hz, P–*C*H–CH), 42.78 (d, $^2J_{PC}$ = 4.3 Hz, P–CH–*C*H), 52.44 and 52.75 (2s, 2 OMe), 119.1 (d, $J$ = 4.5 Hz, OPh, 2 $C_{ortho}$), 119.3 (d, $J$ = 4.6 Hz, OPh, 2 $C_{ortho}$), 124.43 and 124.46 (2s, OPh, 2 $C_{para}$), 128.4 ($CH_{Het}$), 128.5 and 128.7 (2s, OPh, 4 $C_{meta}$), 128.8 ($CH_{Het}$), 139.4 and 143.5 (2 $CH_{Het}$), 144.5 ($C_{Het}$), 148.3 (d, $^2J_{CP}$ = 9.6 Hz, OPh, $C_{ipso}$), 148.7 (d, $^2J_{CP}$ = 8.8 Hz, OPh, $C_{ipso}$), 154.9 ($C_{Het}$), 165.2 (d, $^2J_{PC}$ = 7.4 Hz, CO), 165.9 (d, $^3J_{PC}$ = 19.4 Hz, CO), 179.0 ($NCO_{Het}$). $^{31}$P NMR (161.9 MHz, $CDCl_3$): $\delta_P$ 10.11

*Dimethyl 2-[bis(phenyloxy)phosphoryl]-3-(benzo[d]thiazol-2-thio-S-yl)butandioate (**3b**)*

Yellow powder: yield (0.52 g), mp 152–155 °C, IR (KBr) ($\upsilon_{max}$, $cm^{-1}$): 1733 and 1756 (C = O). Anal. Calcd for $C_{25}H_{22}NO_7PS_2$ (543.55): C, 55.24; H, 4.08; N, 2.58. Found: C, 55.30; H, 4.11; N, 2.61.

$^1$H NMR (400.1 MHz, $CDCl_3$): $\delta_H$ 3.73 and 3.87 (6H, 2s, 2 OMe), 5.64 (1H, dd, $^2J_{HP}$ = 20.8 and $^3J_{HH}$ = 11.1 Hz, P−C*H*−CH), 6.03 (1H, dd, $^3J_{HH}$ = 11.1 and $^3J_{HP}$ = 5.5 Hz, P−CH−C*H*), 7.02–7.35 (10H, m, 2 OPh), 7.31 (1H, d, $^3J_{HH}$ = 7.6 Hz, CH), 7.39 (1H, dt, $J$ = 7.6 and $J$ = 1.2 Hz, CH), 7.44 (1H, dd, $J$ = 7.8 and $J$ = 1.2 Hz, CH), 7.57 (1H, d, $J$ = 8.1 Hz, CH). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta_C$ 42.13 (d, $^1J_{PC}$ = 133.6 Hz, P−*C*H−CH), 46.22 (d, $^2J_{PC}$ = 4.5 Hz, P−CH−*C*H), 52.18 and 52.61 (2s, 2 OMe), 119.1 (d, $J$ = 4.8 Hz, OPh, 2 $C_{ortho}$), 119.2 (d, $J$ = 5.1 Hz, OPh, 2 $C_{ortho}$), 123.9 ($CH_{Het}$), 124.2 and 124.6 (2s, OPh, 2 $C_{para}$), 125.2 ($CH_{Het}$), 128.3 ($CH_{Het}$), 128.6 ($CH_{Het}$), 128.7 and 128.9 (2s, OPh, 4 $C_{meta}$), 140.2 ($CH_{Het}$), 148.9 (d, $^2J_{CP}$ = 8.3 Hz, OPh, $C_{ipso}$), 149.6 (d, $^2J_{CP}$ = 9.4 Hz, OPh, $C_{ipso}$), 154.7 ($C_{Het}$), 168.1 ($NCS_{Het}$), 164.8 (d, $^2J_{PC}$ = 8.1 Hz, CO), 167.4 (d, $^3J_{PC}$ = 18.7 Hz, CO). $^{31}$P NMR (161.9 MHz, $CDCl_3$): $\delta_P$ 10.4

*Dimethyl 2-[bis(phenyloxy)-phosphoryl]-3-(pyridin-2-ylthio)butandioate (**5a**)*

Light yellow viscous oil; IR in $CCl_4$ ($\upsilon_{max}$, $cm^{-1}$): 1701 and 1743 (C = O). MS ($m/z$, %): 488 ($M^+$, 1), 283 (100), 255 (20), 144 (8), 129 (7), 113 (5), 98 (10), 85 (2), 54 (4), 26 (13). Anal. Calcd for $C_{22}H_{21}N_2O_7PS$ (488.45): C, 54.10; H, 4.33; N, 5.74. Found: C, 53.92; H, 4.26; N, 5.78.

*Major isomer:* $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta_H$ 3.73 and 3.78 (6H, 2s, 2 OMe), 4.35 (1H, dd, $^2J_{HP}$ = 24.6 and $^3J_{HH}$ = 6.6 Hz, P–C*H*–CH), 5.81 (1H, dd, $^3J_{HP}$ = 9.5 and $^3J_{HH}$ = 6.6 Hz, P–CH–C*H*), 6.98 (1H, t, $^3J_{HH}$ = 5.0 Hz, 1 $CH_{Het}$), 7.04–7.37 (10H, m, 2 OPh), 8.53 (2H, d, $^3J_{HH}$ = 5.0 Hz, 2 $NCH_{Het}$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta_C$ 42.7 (d, $^2J_{PC}$ = 2.5 Hz, P–CH–*C*H), 46.3 (d, $^1J_{PC}$ = 134.7 Hz, P–*C*H–CH), 52.1 and 52.3 (2s, 2 OMe), 116.1 (s, 1 $CH_{Het}$), 119.6 (d, $^3J_{PC}$ = 5.1 Hz, 2 $CH_{ortho}$), 119.7 (d, $^3J_{PC}$ = 5.3 Hz, 2 $CH_{ortho}$), 124.3 and 124.5 (4 $CH_{meta}$), 128.6 and 128.7 (2 $CH_{para}$), 148.5 (m, 2 $C_{ipso}$), 156.3 and 156.4 (4 $NCH_{Het}$), 164.9 (d, $^3J_{PC}$ = 5.2 Hz, CO), 167.1 (d, $^2J_{PC}$ = 12.1 Hz, CO), 169.7 ($NCN_{Het}$). $^{31}$P NMR (161.9 MHz, $CDCl_3$): $\delta_P$ 12.3

*Minor isomer:* $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta_H$ 3.71 and 3.81 (6H, 2s, 2 OMe), 4.42 (1H, dd, $^2J_{HP} = 24.4$ and $^3J_{HH} = 7.9$ Hz, P–C*H*–CH), 5.35 (1H, dd, $^3J_{HP} = 9.5$ and $^3J_{HH} = 7.9$ Hz, P–CH–C*H*), 7.00 (1H, dd, $^3J_{HH} = 4.8$ and $^3J_{HH} = 4.9$ Hz, 1 $CH_{Het}$), 7.04–7.37 (10H, m, 2 OPh), 8.52 (1H, d, $^3J_{HH} = 4.9$ Hz, 1 $NCH_{Het}$), 8.58 (1H, d, $^3J_{HH} = 4.8$ Hz, 1 $NCH_{Het}$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta_C$ 44.1 (d, $^2J_{PC} = 2.3$ Hz, P–CH–*C*H), 46.7 (d, $^1J_{PC} = 134.5$ Hz, P–*C*H–CH), 51.8 and 52.2 (2s, 2 OMe), 116.3 (s, 1 $CH_{Het}$), 119.4 (d, $^3J_{PC} = 5.5$ Hz, 2 $CH_{ortho}$), 119.8 (d, $^3J_{PC} = 5.3$ Hz, 2 $CH_{ortho}$), 124.4 and 124.8 (4 $CH_{meta}$), 128.9 and 129.0 (2s, 2 $CH_{para}$), 149.0 (m, 2 $C_{ipso}$), 156.5 and 156.9 (4 $NCH_{Het}$), 165.4 (d, $^3J_{PC} = 5.6$ Hz, CO), 166.1 (d, $^2J_{PC} = 12.3$ Hz, CO), 169.4 ($NCN_{Het}$). $^{31}$P NMR (161.9 MHz, $CDCl_3$): $\delta_P$ 12.2

*Diethyl 2-[bis(phenyloxy)-phosphoryl]-3-(pyridin-2-ylthio)butandioate (**5b**)*

Light yellow viscous oil; IR in $CCl_4$ ($\upsilon_{max}$, $cm^{-1}$): 1730 and 1742 (C = O). MS (*m*/*z*, %): 516 ($M^+$, 3), 471 (2), 331 (3), 283 (4), 255 (5), 238 (3), 209 (7), 93 (25), 77 (50), 29 (100). Anal. Calcd for $C_{24}H_{25}N_2O_7PS$ (516.50): C, 55.81; H, 4.88; N, 5.42. Found: C, 55.93; H, 4.78; N, 5.38.

*Major isomer:* $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta_H$ 1.17 (3H, t, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$), 1.21 (3H, t, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$), 4.14 (2H, m, $OCH_2CH_3$), 4.23 (2H, m, $OCH_2CH_3$), 4.33 (1H, dd, $^2J_{HP} = 24.5$ and $^3J_{HH} = 7.0$ Hz, P–C*H*–CH), 5.77 (1H, dd, $^3J_{HP} = 9.4$ and $^3J_{HH} = 7.0$ Hz, P–CH–C*H*), 6.95 (1H, t, $^3J_{HH} = 4.5$ Hz, 1 $CH_{Het}$), 7.09–7.34 (10H, m, 2 OPh), 8.49 (2H, d, $^3J_{HH} = 4.5$ Hz, 2 $NCH_{Het}$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta_C$ 12.7 and 12.8 (2s, 2 $OCH_2CH_3$), 42.7 (d, $^2J_{PC} = 2.1$ Hz, P–CH–*C*H), 46.3 (d, $^1J_{PC} = 135.4$ Hz, P–*C*H–CH), 61.2 and 61.3 (2s, 2 $OCH_2CH_3$), 116.0 (s, 1 $CH_{Het}$), 119.5 (d, $^3J_{PC} = 4.3$ Hz, 2 $CH_{ortho}$), 119.6 (d, $^3J_{PC} = 4.4$ Hz, 2 $CH_{ortho}$), 124.2 and 124.4 (4 $CH_{meta}$), 128.5 and 128.6 (2s, 2 $CH_{para}$), 148.9 (m, 2 $C_{ipso}$), 165.1 (d, $^3J_{PC} = 5.2$ Hz, CO), 165.1 and 165.2 (4 $NCH_{Het}$), 168.9 ($NCN_{Het}$), 169.0 (d, $^2J_{PC} = 12.3$ Hz, CO). $^{31}$P NMR (161.9 MHz, $CDCl_3$): $\delta_P$ 12.7

*Minor isomer:* $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta_H$ 1.16 (3H, t, $^3J_{HH} = 7.0$ Hz, $OCH_2CH_3$), 1.26 (3H, t, $^3J_{HH} = 7.1$ Hz, $OCH_2CH_3$), 4.20–4.27 (4H, m, 2 $OCH_2CH_3$), 4.38 (1H, dd, $^2J_{HP} = 24.4$ and $^3J_{HH} = 7.9$ Hz, P–C*H*–CH), 5.34 (1H, dd, $^3J_{HP} = 9.6$ and $^3J_{HH} = 7.9$ Hz, P–CH–C*H*), 6.92 (1H, t, $^3J_{HH} = 4.8$ Hz, 1 $CH_{Het}$), 7.09–7.34 (10H, m, 2 OPh), 8.38 (2H, d, $^3J_{HH} = 4.8$ Hz, 2 $NCH_{Het}$). $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta_C$ 12.8 and 12.9 (2s, 2 $OCH_2CH_3$), 44.1 (d, $^2J_{PC} = 2.5$ Hz, P–CH–*C*H), 46.5 (d, $^1J_{PC} = 134.9$ Hz, P–*C*H–CH), 61.4 and 61.3 (2s, 2 $OCH_2CH_3$), 115.9 (s, 1 $CH_{Het}$), 119.3 (d, $^3J_{PC} = 4.7$ Hz, 2 $CH_{ortho}$), 119.5 (d, $^3J_{PC} = 4.4$ Hz, 2 $CH_{ortho}$), 124.1 and 124.2 (4 $CH_{meta}$), 128.5 and 128.7 (2s, 2 $CH_{para}$), 148.9 (m, 2 $C_{ipso}$), 165.1 and 165.2 (4 $NCH_{Het}$), 165.5 (d, $^3J_{PC} = 5.1$ Hz, CO), 168.1 (d, $^2J_{PC} = 12.0$ Hz, CO), 168.7 ($NCN_{Het}$). $^{31}$P NMR (161.9 MHz, $CDCl_3$): $\delta_P$ 12.6



## Acknowledgements

We gratefully acknowledge financial support from the Research Council of Islamic Azad University of Khoy and The University of Sistan & Baluchestan.

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