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Synthesis of New Phosphonato Esters by Reaction between Triphenyl or Trialkyl Phosphite and Acetylenic Diesters in the Presence of NH-Containing Compounds

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ABSTRACT: *The reaction between triphenyl or trialkyl phosphite and acetylenic esters in the presence of some heterocyclic or aromatic NH compounds such as thiazolidine-2,4-dione, 2-methyl indole, 5-bromoisatine, 3-nitroacetanilide, saccharin, 5,5-dimethylhydantoin, 2-nitroaniline, 4-nitroaniline, benzophenon hydrazine, and anthranilic acid led to the formation of phosphonato esters in high yield.* Heteroatom Chem 22:630–639, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20725

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INTRODUCTION

Heterocyclic systems with oxygen, nitrogen, sulfur, and other heteroatoms in five- and six-membered rings, and also phosphorus compounds, are of interest due to their pharmaceutical and biological activities such as anti-inflammatory, cardiotonic, inotropic, antihypertensive, antimicrobial, and antibacterial properties [1–15]. Numerous studies have been previously reported 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 [16–30].

Continuing a series of investigations made on the development of organophosphorus heterocyclic compound synthesis [22–30], we now describe a one-pot synthesis of heterocyclic and aromatic phosphonato ester derivatives **4a–f, 5a–g**, and **7**, using

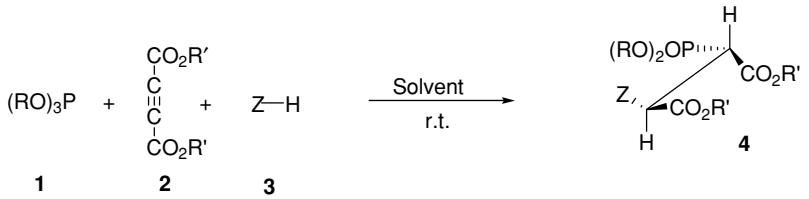
triphenyl or trialkyl phosphite **1** and acetylenic diesters **2** in the presence of NH heterocyclic or aromatic compounds **3** and**6**.

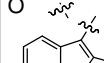
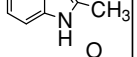
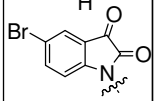
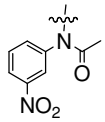
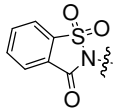
RESULTS AND DISCUSSION

The aim of this work was to undertake the reactions between triphenyl or ethyl phosphite **1** and acetylenic diesters **2** in the presence of heterocyclic or aromatic NH compounds **3** in appropriate solvents. These reactions preceded smoothly at room temperature and were completed within 2–48 h and resulted in high yields. TLC monitoring and ^{1}H NMR spectra of the crude products clearly indicated formation of phosphonate esters **4** (see Schemes 1 and 2).

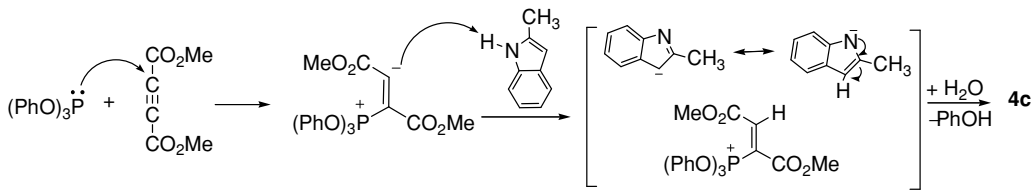
The essential structures of the products **4a–f, 5a–f**, and **7** were deduced from elemental analysis, IR, ^{1}H, ^{13}C, and ^{31}P NMR, and mass spectra. The mass spectra of these compounds displayed molecular ion peaks at appropriate *m/z* values, in addition to molecular fragmentation peaks involving the loss of the ester and phenoxy or alkoxy moieties. No products other than **4a–f, 5a–f**, and **7** could be detected by NMR spectroscopy.

The ^{1}H NMR spectra of **4a** showed two singlets (at $\delta = 3.75$ and 3.87 ppm) for methoxy protons, an AB quartet ($\delta = 3.97$, $^2J_{HH} = 17.3$ Hz) for the methylene group and a multiplet ($\delta = 7.10$–7.37 ppm) for aromatic protons. In addition, two doublet of doublets were observed for the vicinal methine protons of **4a** ($\delta = 4.45$, $^3J_{HH} = 11.5$, $^2J_{HP} = 21.1$ Hz, and $\delta = 5.87$, $^3J_{HH} = 11.5$, $^3J_{HP} = 4.8$ Hz), respectively. The vicinal proton–proton coupling constant ($^3J_{HH}$) can be obtained from the Karplus equation as a function of the torsion angle [31–35]. Typically J_{gauche}

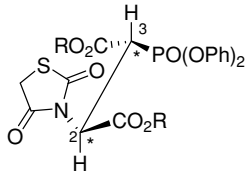


4	R	R′	Z	Solvent	% Yield
a	Ph	Me		Diethyl ether	97
b	Ph	Et		Diethyl ether	94
c	Ph	Me		DMF	90
d	Ph	Me		DMF	93
e	Et	Me		EtoAc	91
f	Me	Me		1 : 1 Ether : EtoAc	94

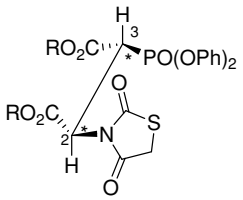
SCHEME 1



SCHEME 2



(2*R*, 3*R*)-**4a** or (2*S*, 3*S*)-**4a**



(2*S*, 3*R*)-**4a** or (2*R*, 3*S*)-**4a**

SCHEME 3

and J_{anti} configurations give rise to distinct coupling constants, which vary between 1.5–5 and 10–14 Hz, respectively [31–35]. The observation of $^3J_{HH} = 11.5$ Hz for the vicinal methine protons in compound **4a** confirms an anti arrangement for these protons. Since compounds possess two stereogenic centers, two diastereoisomers [(2*R*, 3*R*)-**4** or (2*S*, 3*S*)-**4** and (2*S*, 3*R*)-**4** or (2*R*, 3*S*)-**4**] with an anti *HCCH* arrangement are possible (Scheme 3). In addition, compound **4d** showed two broad peaks for vicinal methine protons (P-C*H*-C*H*), such that we were unable to recognize the configuration of these protons.

The presence of phosphorus (^{31}P) nucleus in the compounds **4** assist in identifying their configuration by analysis of the long-range spin–spin coupling signals of phosphorus (^{31}P) nucleus with the neighboring protons (^{1}H) and carbon (^{13}C) nuclei (see the Experimental section).

The carbon–phosphorus three bond range coupling constant $^3J_{CP}$ is associated with the anti or cis configuration (transoid coupling being larger than cisoid coupling) [31]. The Karplus relationship can be derived from the literature data for organophosphorus compounds with tetra- or pentavalent phosphorus environments [32]. The observation of $^3J_{CP} = 19.1$ Hz at $\delta = 166.28$ ppm for the ester carbonyl group of compounds **4a** is in agreement with an anti-arrangement along the P-CH-CH-CO bond. This assignment was reinforced in **4a** with the smaller coupling of the phosphorus to the proximal ester carbon group, $^2J_{CP} = 8.1$ Hz at $\delta = 165.18$ ppm.

In a series of other experiments, from reactions between triphenyl phosphite and acetylenic diesters in the presence of 2-nitroaniline, 4-nitroaniline, anthranilic acid, *o*-trifluoromethylaniline, diphenylhydrazone, or 5,5-dimethylhydantoin, the hitherto unknown butanedioates **5** and **7** were generated in 91–95% yield. All compounds are stable, with the proposed structures being fully supported by elemental analyses and IR, ^{1}H, ^{13}C, and ^{31}P NMR, and mass spectroscopy data. The mass spectra of these 1:1:1 adducts displayed fairly weak molecular ion peaks (Scheme 4).

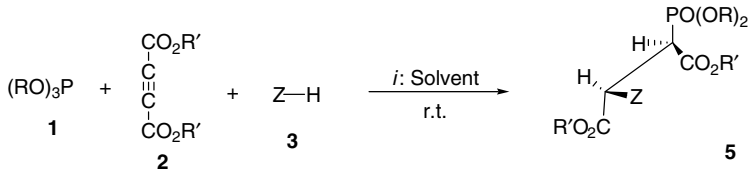
When the reaction between triphenyl phosphite and acetylenic esters in the presence of 2-nitroaniline was conducted, only one diastereoisomer was obtained for compounds **5 (a**,**b, e**, and **f**), since compounds **5** (**c,d**, and **g**) and **7** consist of a mixture of two diastereoisomers (see the Experimental section).

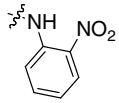
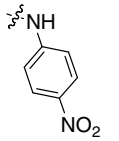
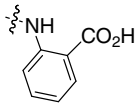
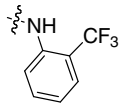
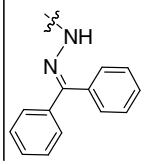
The observation of $^3J_{HH} = 3.6$ and 3.7 Hz for the vicinal protons in compounds **5a** and **5b** confirms a gauche-arrangement for these protons, respectively. Since compounds **5a** and **5b** possess two stereogenic centers, two diastereoisomers, [(2*R*, 3*R*) or (2*S*, 3*S*)] and [(2*R*, 3*S*) or (2*S*, 3*R*)] with a *gauche HCCH* arrangement are possible (Scheme 5). For example, the ^{1}H NMR spectrum of **5c** displays double doublets and a double doublets of doublets for the vicinal protons of the major isomer and also a double doublets and a multiplet for the vicinal protons of the minor isomer: ($\delta = 4.22$, $^3J_{HH} = 3.6$, $^2J_{HP} = 25.4$ Hz, and $\delta = 4.96$, $^3J_{HH} = 3.6$, $^3J_{HP} = 7.7$ Hz) and ($\delta = 4.10$, $^3J_{HH} = 5.1$, $^2J_{HP} = 24.4$ Hz, and $\delta = 5.10$), respectively.

In addition, two diastereoisomers in compound **7** with *anti* and *gauche HCCH* arrangement are possible (Scheme 6 and 7). Attempts to separate the major and the minor compounds **5 (c, d**, and **g**) and **7** were unsuccessful. Single-crystal X-ray diffraction was used to authenticate the structure of compound **5e** (Fig. 1). Prismatic colorless crystals of **5e** were prepared by slow evaporation of a saturated solution of dichloromethane.

On the basis of the proposed mechanism in the literature [36–40], it is reasonable to assume that the heterocyclic phosphonato ester **4** results from the initial addition of triphenyl phosphite **1** to the acetylenic ester **2** (1:1 adduct or zwitterionic **A**), with subsequent protonation of the 1:1 adduct by the NH compound **3** to generate the intermediate phosphonium ion **B**, which was followed by q reaction with the conjugate base ($\mathbf{Z}^-$) to produce the ylide **C**. It is converted to **D** in the presence of moisture and with subsequent loss of PhOH (see Scheme 8).

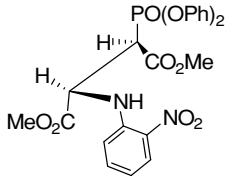
In conclusion, the reaction between triphenyl or triethyl phosphite and acetylenic esters in the presence of NH compounds, such as thiazolidine-2,4-dione, 2-methyl indole, 5-bromoisatine, 3-nitroacetanilide, saccharin, 5,5-dimethylhydantoin, 2-nitroaniline, 4-nitroaniline, benzophenon hydrazine, and anthranilic acid, provides a simple one-pot entry into the synthesis of stable phosphonato esters of potential interest. The present procedure has the advantage that not only is the reaction performed



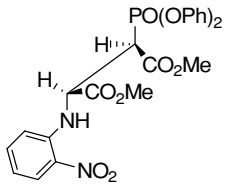
5	R	R′	Z	Solvent	% Yield
a	Ph	Me		EtoAc	95[a]
b	Ph	Et		Et_2O	91[a]
c	Ph	Me		Et_2O	93[b]
d	Ph	Et		1:1 Et_2O/*n*-Hexane	92[b]
e	Ph	Me		Acetone	95[a]
f	Ph	Me		EtOAc	95[a]
g	Ph	Me		EtOAc	93[b]

[a] Only one isomer with gauche HCCH arrengement.
[b] Mixture of two isomer with gauche HCCH arrengement.

SCHEME 4



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



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

SCHEME 5

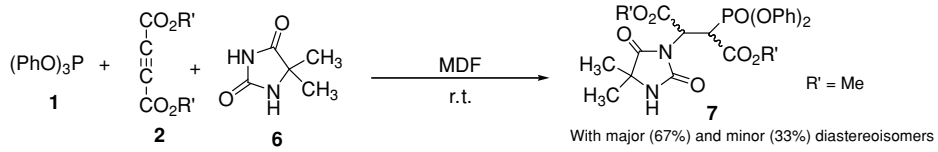
under neutral conditions but also the substances can be mixed without any activation or modifications.

EXPERIMENTAL

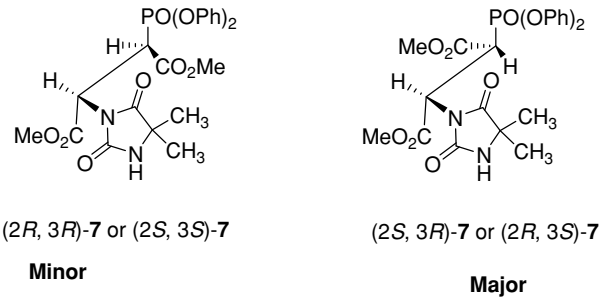
Melting points and IR spectra were measured on an Electrothermal 9100 apparatus (England) and a JASCO FT-IR 460 plus spectrometer (Japan), respectively. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DRX-300 and 400 Avance instrument (Germany) with $CDCl_3$ as a solvent at 400.1, 100.6, and 161.9 MHz, respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer (Germany). The mass spectra were recorded on a Shimadzu GCMS-QP5050A (Japan) mass spectrometer operating at an ionization potential of 70 eV. Triphenyl phosphite, dialkyl acetylendicarboxylate, thiazolidine-2,4-dione, 2-methyl indole, 5-bromoisatine, 3-nitroacetanilide, saccharin, 5,5-dimethylhydantoin, 2-nitroaniline, 4-nitroaniline, benzophenon hydrazine, and anthranilic acid were purchased from Merck (Darmstadt, Germany), Fluka (Buchs, Switzerland), and Acros (Geel, Belgium), and used without further purifications.

General Procedure (Exemplified by **4a***)*

To a stirred solution of thiazolidine-2,4-dione (1 mmol) and dimethyl acetylendicarboxylate (1 mmol) in 10 mL diethyl ether, a mixture of triphenyl phosphite (1 mmol) in 5 mL diethyl ether was added drop



SCHEME 6



SCHEME 7

wise at −5°C over 10 min. The mixture was then allowed to warm up to room temperature and was stirred for 5 h. The solvent was removed under reduced pressure, and the residue was washed by diethyl ether (2×3) mL to afford the pure product.

*(2R, 3S)-Dimethyl 2-(2,4-thiazolindione-N-yl)-3-(diphenoxyphosphoryl)butandioate (**4a**)*

White powder; yield: 97% (0.48 g), mp = 85–88°C. IR (KBr) (ν_{max}, cm^{-1}): 1766, 1745, and 1690 (C=O), 1288 (P=O). MS (*m/z*, %): 493 (M^+, 1), 462 (4), 434 (1), 400 (100), 376 (7), 346 (4), 285 (30), 94 (16), 77 (51). Anal. Calcd for $C_{21}H_{20}NO_9PS$ (493.42): C, 51.12; H, 4.09; N, 2.84. Found: C, 51.25; H, 4.03; N, 2.93.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 3.75 and 3.87 (6H, 2s, 2 OCH_3), 3.97, (AB quartet $^2J_{HH}$ = 17.3 Hz, SCH_2CO), 4.45 (1H, dd, $^3J_{HH}$ = 11.5, $^2J_{PH}$ = 21.1 Hz, PC*H*CH), 5.87 (1H, dd, $^3J_{HH}$ = 11.5, $^3J_{PH}$ = 4.8 Hz, PCHC*H*), 7.10–7.37 (10H, m, 2OPh).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 32.51 (s, S*C*H_2CO), 42.43 (d, $^1J_{PC}$ = 133.8 Hz, P*C*HCH), 50.64 (d, $^2J_{PC}$ = 4.2 Hz, PCH*C*H), 52.35 and 52.66 (2s, 2O*C*H_3), 119.24 (d, $^3J_{PC}$ = 4.4 Hz, $2C_{ortho}$), 119.50 (d, $^3J_{PC}$ = 4.2 Hz, $2C_{ortho}$), 124.67 and 124.80 (2s, $2C_{para}$),

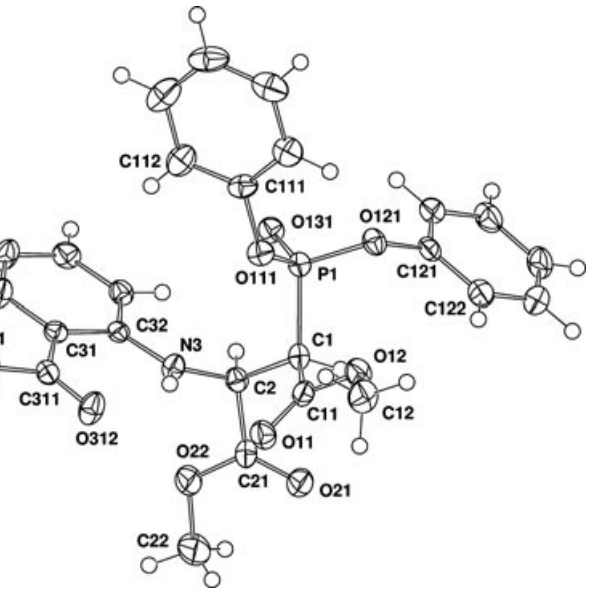
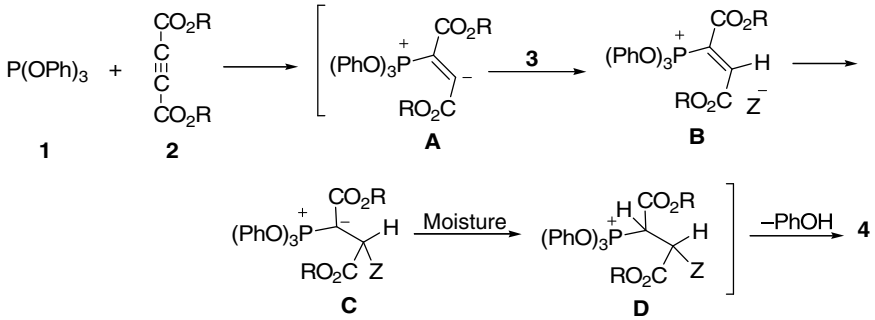


FIGURE 1 Crystal structure of **5e** with ellipsoids depicted at the 50% probability level. Hydrogen atoms have been drawn with arbitrary radii.



SCHEME 8

128.81 and 128.84 (2s, 4C_{meta}), 148.25 (d, $^2J_{PC}$ = 10.2 Hz, C_{ipso}), 148.80 (d, $^2J_{PC}$ = 8.5 Hz, C_{ipso}), 165.18 (d, $^2J_{PC}$ = 8.1 Hz, CO), 166.28 (d, $^3J_{PC}$ = 19.1 Hz, CO), 167.88 (s, N*C*O), 169.73 (s, S*C*ON). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ_P 9.44.

*(2R, 3S)-Dimethyl 2-(2,4-thiazolindione-N-yl)-3-(diphenoxyphosphoryl)butandioate (***4b***)*

White powder; yield: 94% (0.49 g), mp = 103.5–106°C. IR (KBr) (ν_{max}, cm^{-1}): 1749 and 1696 (C=O), 1273 (P=O). MS (*m/z*, %): 522 (M^+ +1, 3), 521 (M^+, 1), 476 (10), 428 (100), 380 (19), 311 (60), 297 (2), 255 (94), 227 (5), 94 (26), 77 (58). Anal. Calcd for $C_{23}H_{24}NO_9PS$ (521.48): C, 52.97; H, 4.64; N, 2.69. Found: C, 53.08; H, 4.59; N, 2.74.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.27 (3H, t, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 1.35 (3H, t, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 3.96–4.04 (2H, m, SCH_2CO), 4.16–4.34 (3H, m, OCH_2CH_3), 4.36 (1H, q, $^3J_{HH}$ = 7.1 Hz, OCH_2CH_3), 4.45 (1H, dd, $^3J_{HH}$ = 11.5, $^2J_{PH}$ = 21.1 Hz, PC*H*CH), 5.87 (1H, dd, $^3J_{HH}$ = 11.5, $^3J_{PH}$ = 4.7 Hz, PCHC*H*), 7.14–7.36 (10H, m, 2OPh).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_P 13.96 and 14.00 (2s, 2 OCH_2CH_3), 33.57 (s, SCH_2CO), 43.71 (d, $^1J_{PC}$ = 133.1 Hz, P*C*HCH), 51.86 (d, $^2J_{PC}$ = 4.5 Hz, PCH*C*H), 62.52 and 63.03 (2s, 2O*C*H_2CH_3), 120.33 (d, $^3J_{PC}$ = 4.3 Hz, 2C_{ortho}), 120.61 (d, $^3J_{PC}$ = 4.3 Hz, 2C_{ortho}), 125.64 and 125.77 (2s, 2C_{para}), 129.85 and 129.87 (2s, 4C_{meta}), 149.41 (d, $^2J_{PC}$ = 10.3 Hz, C_{ipso}), 150.00 (d, $^2J_{PC}$ = 8.5 Hz, C_{ipso}), 165.72 (d, $^2J_{PC}$ = 7.9 Hz, CO), 166.74 (d, $^3J_{PC}$ = 19.1 Hz, CO), 170.53 (br s, N*C*O), 170.85 (s, S*C*ON). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ_P 9.81.

*(2S, 3R)-Dimethyl 2-(2-methyl-1H-indol-3-yl)-3-(diphenoxyphosphoryl)butandioate (***4c***)*

Brown viscous oil; yield: 90% (0.46 g), IR (in CCl_4) (ν_{max}, cm^{-1}): 3309 (NH), 1743 and 1691 (C=O), 1254 (P=O). MS (*m/z*, %): 507 (M^+, 3), 475 (1), 411 (7), 376 (2), 351 (1), 326 (88), 94 (100). Anal. Calcd for $C_{27}H_{26}NO_7P$ (507.47): C, 63.90; H, 5.16; N, 2.76. Found: C, 63.84; H, 5.11; N, 2.84.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 2.38 (3H, s, CH_3), 3.60 and 3.80 (6H, 2s, 2O*C*H_3), 4.56 (1H, dd, $^3J_{HH}$ = 11.9, $^2J_{PH}$ = 22.5 Hz, PC*H*CH), 4.93 (1H, $^3J_{HH}$ = 11.9, $^3J_{PH}$ = 9.4 Hz, PCHC*H*), 6.50–7.72 (14H, m, 2 OPh and 4 CH_{arom}).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 11.93 (s, -*C*H_3), 41.86 (d, $^2J_{PC}$ = 4.0 Hz, PCH*C*H), 47.23 (d, $^1J_{PC}$ = 136.9 Hz, P*C*HCH), 52.60 and 53.10 (2s, 2O*C*H_3), 118.42 and 119.72 (2CH_{arom}), 119.75 (d, $^3J_{PC}$ = 4.8 Hz, 2C_{ortho}), 120.13 (d, $^3J_{PC}$ = 4.8 Hz, 2C_{ortho}), 120.24, 120.72, 123.71 and 124.88 (2CH and 3C_{arom}), 125.22 and 125.24 (2s, 2C_{para}), 126.61 (C_{arom}), 129.43 and 129.47 (2s, 4C_{meta}), 149.78 and 152.59 (2d, $^2J_{PC}$ = 9.1 Hz, 2C_{ipso}), 152.65 (C_{arom}), 168.66 (d, $^2J_{PC}$ = 5.0 Hz, CO), 172.69 (d, $^3J_{PC}$ = 22.8 Hz, CO). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ_P 13.42.

*(2R, 3S)-Dimethyl 2-(5-bromo-2,3-dioxoindolin-1-yl)-3-(diphenoxyphosphoryl)butandioate (***4d***)*

Brown viscous oil; yield: 93% (0.56 g), IR (in CCl_4) (ν_{max}, cm^{-1}): 1750 and 1609 (C=O), 1235 (P=O). MS (*m/z*, %): 604 (M^++2, 5), 603 (M^+ +1, 3), 602 (M^+, 5), 510 (72), 508 (67), 377 (8), 349 (8), 285 (25), 250 (91), 94 (100), 77 (78). Anal. Calcd for $C_{26}H_{21}BrNO_9P$ (602.32): C, 51.85; H, 3.51; N, 2.33. Found: C, 51.96; H, 3.44; N, 2.19.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 3.75 and 3.88 (6H, 2s, 2 O*C*H_3), 5.33 and 6.53 (2H, 2 br s, PC*H*CH and PCHC*H*), 6.56–7.63 (13H, m, 2OPh and 3CH_{arom}).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 42.11 (d, $^1J_{PC}$ = 133.7 Hz, P*C*HCH), 48.16 (d, $^2J_{PC}$ = 5.3 Hz, PCH*C*H), 53.54 and 53.87 (2s, 2O*C*H_3), 117.03 and 119.27 (2s, 2CH_{arom}), 120.15 (d, $^3J_{PC}$ = 4.8 Hz, 2C_{ortho}), 120.26 (d, $^3J_{PC}$ = 4.8 Hz, 2C_{ortho}), 124.00 (s, 2C_{para}), 125.70 and 125.82 (2s, CH and C_{arom}), 125.22 and 125.24 (2s, 2C_{para}), 126.61 (C_{arom}), 129.45 and 129.53 (2s, 4C_{meta}), 129.94 (s, C_{arom}), 149.13 (d, $^2J_{PC}$ = 9.3 Hz, C_{ipso}), 151.28 (d, $^2J_{PC}$ = 9.1 Hz, C_{ipso}), 156.00 (CO), 167.85 (d, $^2J_{PC}$ = 7.5 Hz, CO), 168.14 (d, $^3J_{PC}$ = 21.5 Hz, CO), 180.12 (CO). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ_P 10.05.

*(2S, 3R)-Dimethyl 2-[N-(3-nitrophenyl)acetamido]-3-(diethoxyphosphoryl)butandioate (***4e***)*

Yellow crystalline; yield: 91% (0.42 g), mp = 126–129°C. IR (KBr) (ν_{max}, cm^{-1}): 1740 and 1734 (C=O), 1229 (P=O). MS (*m/z*, %): 461 (M^+ +1, 4), 460 (M^+, 1), 429 (3), 414 (2), 400 (4), 359 (82), 281 (26), 265 (3), 235 (13), 221 (100). Anal. Calcd for $C_{18}H_{25}N_2O_{10}P$ (460.37): C, 46.96; H, 5.47; N, 6.08. Found: C, 46.89; H, 5.51; N, 6.13.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.16 and 1.25 (6H, 2t, $^3J_{HH}$ = 7.1 Hz, 2OCH_2CH_3), 1.93 (3H, s, $NCOCH_3$), 3.79 and 3.82 (6H, 2s, 2O*C*H_3), 3.97–4.17 (4H, 2m, 2ABX_3 system, 2O*C*H_2CH_3), 4.44 (1H, dd, $^3J_{HH}$ = 10.0, $^2J_{PH}$ = 20.7 Hz, PC*H*CH), 4.81 (1H, dd, $^3J_{HH}$ = 10.0, $^3J_{PH}$ = 4.4 Hz, PCHC*H*), 6.64 (1H, t, *J* = 8.1 Hz, CH), 8.07 (1H, d, *J* = 7.9 Hz, CH), 8.24 (1H, dd, *J* = 8.2 and 1.6 Hz, CH), 8.53 (1H, t, *J* = 2.0 Hz, CH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 15.74 (d, $^3J_{PC}$ = 6.3 Hz, $POCH_2CH_3$), 15.84 (d, $^3J_{PC}$ = 6.4 Hz, $POCH_2CH_3$), 22.60 (s, $NCOCH_3$), 44.78 (d, $^1J_{PC}$ = 130.0 Hz, P*C*HCH), 51.89 (d, $^2J_{PC}$ = 6.3 Hz, PCH*C*H), 52.63 and 53.00 (2s, 2O*C*H_3), 62.70 (d, $^2J_{PC}$ = 7.1 Hz,

POCH_2CH$_3$), 63.25 (d, $^2J_{PC}$ = 6.4 Hz, POCH_2CH$_3$), 112.56, 123.19, 129.84, 134.28, 144.82 and 148.38 (6s, CH and C_{arom}), 167.90 (d, $^2J_{PC}$ = 6.9 Hz, CO), 169.46 (d, $^3J_{PC}$ = 18.1 Hz, CO), 171.10 (NCO). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ_P 17.80.

*(2S, 3R)-Dimethyl 2-(1,2-dihydro-1λ^6-benzol[d]-isothiazol-3-one-2-yl)–3-(dimethoxyphosphoryl) butandioate (**4f**)*

White powder; yield: 94% (0.41 g), mp = 125–127°C. IR (KBr) (ν_{max}, cm^{-1}): 1738 and 1721 (C=O), 1259 (P=O). MS (*m/z*, %): 436 (M +1, 3), 435 (M$^+$, 2), 404 (9), 376 (73), 221 (76), 193 (100), 109 (95), 59 (24). Anal. Calcd for (435.34): $C_{15}H_{18}NO_{10}PS$: C, 41.38; H, 4.17; N, 3.22. Found: C, 41.23; H, 4.10; N, 3.31.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 3.71–3.86 (12H, m, 4OCH_3), 4.40 (1H, dd, $^3J_{HH}$ = 11.4, $^2J_{PH}$ = 21.1 Hz, PC*H*CH), 5.53 (1H, dd, $^3J_{HH}$ = 11.4, $^2J_{PH}$ = 7.3 Hz, PCHC*H*), 7.82–8.11 (4H, m, CH_{arom}).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 43.49 (d, $^1J_{PC}$ = 129.7 Hz, P*C*HCH), 50.82 (d, $^2J_{PC}$ = 4.6 Hz, PCH*C*H), 53.18, 53.45, 53.54 and 53.72 (4s, 4O*C*H$_3$), 121.09, 125.51, 126.71, 134.41, 135.10, and 137.90 (6s, CH and C_{arom}), 159.40 (s, S*C*ON), 167.34 (d, $^2J_{PC}$ = 7.2 Hz, CO), 167.56 (d, $^3J_{PC}$ = 7.5 Hz, CO). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ_P 18.57.

*(2R,3R)-Dimethyl 2-(2-nitrophenylamino)-3-(diphenoxyphosphoryl)butandioate (**5a**)*

Yellow powder; yield: 95% (0.49 g), mp = 97–100°C. IR (KBr) (ν_{max}, cm^{-1}): 3339 (NH), 1731 and 1711 (C=O), 1282 (P=O). MS (*m/z*, %): 514 (M$^+$, 11), 455 (59), 423 (47), 376 (29), 317 (21), 283 (76), 223 (83), 138 (100), 92 (43), 77 (64), 65 (69). Anal. Calcd for $C_{24}H_{23}N_2O_9P$ (514.42): C, 56.04; H, 4.51; N, 5.45. Found: C, 55.98; H, 4.42; N, 5.61.

^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 3.59 and 3.72 (6H, 2s, 2OCH_3), 4.28 (1H, dd, $^3J_{HH}$ = 3.6, $^2J_{PH}$ = 25.5 Hz, PC*H*CH), 5.15 (1H, ddd, $^3J_{HH}$ = 3.6, $^3J_{PH}$ = 8.0, $^3J_{HH}$ = 10.5 Hz, PC*H*CH), 6.71 (1H, dt, J_{HH} = 1.2, J_{HH} = 7.6 Hz, CH_{arom}), 6.94–7.44 (12H, m, 2OPh and 2CH_{arom}), 8.10 (1H, dd, J_{HH} = 1.5, J_{HH} = 8.5 Hz, CH_{arom}), 9.12 (1H, d, J_{HH} = 10.5 Hz, NH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 47.05 (d, $^1J_{PC}$ = 136.2 Hz, P*C*HCH), 53.39 and 53.53 (2s, 2O*C*H$_3$), 53.80 (d, $^2J_{PC}$ = 3.1 Hz, PCH*C*H), 114.71 and 117.03 (2s, 2*C*H$_{arom}$), 120.00 (d, $^3J_{CP}$ = 4.8 Hz, 2*C*H$_{ortho}$), 120.71 (d, $^3J_{CP}$ = 4.5 Hz, 2*C*H$_{ortho}$), 126.60 (CH_{arom}), 125.29 and 125.88 (2s, 2C_{para}), 129.46 and 130.00 (2s, 4C_{meta}), 133.58 and 135.97 (2s, CH and C_{arom}), 143.88 (s, C_{arom}), 149.71 (d, $^2J_{CP}$ = 8.8 Hz, 2C_{ipso}), 167.09 (d, $^2J_{PC}$ = 5.4 Hz, CO), 170.55 (d, $^3J_{PC}$ = 18.2 Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 11.74.

*(2R,3R)-Diethyl 2-(2-nitrophenylamino)-3-(diphenoxyphosphoryl)butandioate (**5b**)*

Yellow powder; yield: 91% (0.49 g), mp = 84–86°C. IR (KBr) (ν_{max}, cm^{-1}): 3359 (NH), 1726 and 1707 (C=O), 1268 (P=O). MS (*m/z*, %): 542 (M$^+$, 10), 469 (100), 423 (51), 331 (20), 275 (35), 138 (63), 92 (36), 77 (40), 65 (43). Anal. Calcd for $C_{26}H_{27}N_2O_9P$ (542.47): C, 57.57; H, 5.02; N, 5.16. Found: C, 57.49; H, 5.11; N, 5.24.

^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 1.19 (3H, t, J = 7.1 Hz, OCH_2CH_3), and 1.41 (3H, t, J = 7.2 Hz, OCH_2CH_3), 4.12–4.18 (2H, m, OCH_2CH$_3$), 4.26 (1H, dd, $^3J_{HH}$ = 3.7, $^2J_{PH}$ = 25.6 Hz, PC*H*CH), 4.34–4.47 (2H, m, OCH_2CH$_3$), 5.09 (1H, ddd, $^3J_{HH}$ = 3.6, $^3J_{PH}$ = 7.7, $^3J_{HH}$ = 10.9 Hz, PC*H*CH), 6.70 (1H, dt, J_{HH} = 1.0, J_{HH} = 7.15 Hz, CH_{arom}), 6.93–7.43 (12H, m, 2OPh and 2CH_{arom}), 8.08 (1H, dd, J_{HH} = 1.36, J_{HH} = 8.6 Hz, CH_{arom}), 9.06 (1H, br d, J_{HH} = 10.9 Hz, NH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 13.59 and 14.10 (2s, 2OCH$_2$*C*H$_3$), 47.21 (d, $^1J_{PC}$ = 136.3 Hz, P*C*HCH), 54.09 (d, $^2J_{PC}$ = 3.3 Hz, PCH*C*H), 62.90 and 62.47 (2s, 2O*C*H$_2$CH$_3$), 115.02 and 117.02 (2s, 2*C*H$_{arom}$), 120.02 (d, $^3J_{CP}$ = 4.8 Hz, 2*C*H$_{ortho}$), 120.78 (d, $^3J_{CP}$ = 4.3 Hz, 2*C*H$_{ortho}$), 126.53 (CH_{arom}), 125.81 and 125.93 (2s, 2C_{para}), 129.41 and 129.97 (2s, 4C_{meta}), 133.66 and 135.87 (2s, CH and C_{arom}), 144.14 (s, C_{arom}), 149.75 (d, $^2J_{CP}$ = 8.2 Hz, C_{ipso}), 149.82 (d, $^2J_{CP}$ = 8.3 Hz, C_{ipso}), 166.40 (d, $^2J_{PC}$ = 5.4 Hz, CO), 170.01 (d, $^3J_{PC}$ = 18.4 Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 12.24.

*Dimethyl 2-(4-nitrophenylamino)-3-(diphenoxyphosphoryl)butandioate (**5c**)*

Pale yellow powder; yield: 93% (0.48 g), mp = 129–132°C. IR (KBr) (ν_{max}, cm^{-1}): 3368 and 3286 (2NH), 1733 and 1730 (C=O), 1266 (P=O). MS (*m/z*, %): 514 (M$^+$, 11), 455 (24), 423 (15), 376 (31), 283 (73), 223 (100), 138 (40), 77 (64). Anal. Calcd for $C_{24}H_{23}N_2O_9P$ (514.42): C, 56.04; H, 4.51; N, 5.45. Found: C, 56.13; H, 4.66; N, 5.31.

Major isomer (69%): ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 3.73 and 3.92 (6H, 2s, 2OCH_3), 4.22 (1H, dd, $^3J_{HH}$ = 3.6, $^2J_{PH}$ = 25.4 Hz, PC*H*CH), 4.96 (1H, ddd, $^3J_{HH}$ = 3.6, $^3J_{PH}$ = 7.7, $^3J_{HH}$ = 10.9 Hz, PCHC*H*), 5.73 (1H, d, $^3J_{HH}$ = 10.9 Hz, N*H*), 6.55–8.05 (14H, m, 2OPh and 4CH_{arom}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 47.00 (d, $^1J_{PC}$ = 138.5 Hz, P*C*HCH), 53.35 and 53.55 (2s, 2O*C*H$_3$), 54.31 (d, $^2J_{PC}$ = 3.2 Hz, PCH*C*H), 112.77 (s, CH_{arom}), 120.21 and 120.59 (2d, $^3J_{PC}$ = 4.5 Hz, 4C_{ortho}), 125.57 and 125.96 (2s, 2C_{para}), 125.98 (s, CH_{arom}), 129.73 and 130.00 (2s, 4C_{meta}), 139.48 (s, C_{arom}), 149.61 and 149.84 (2d, $^2J_{PC}$ = 8.8 Hz, 2 C_{ipso}),

151.87 (s, C_{arom}), 168.08 (d, $^2J_{PC} = 5.3$ Hz, CO), 170.67 (d, $^3J_{PC} = 18.2$ Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 11.29.

Minor isomer (31%): ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 3.72 and 3.82 (6H, 2s, 2OC*H*$_3$), 4.10 (1H, dd, $^3J_{HH} = 5.1$, $^2J_{PH} = 24.4$ Hz, PC*H*CH), 5.06 (1H, m, PCHC*H*), 5.50 (1H, d, $^3J_{HH} = 8.6$ Hz, N*H*), 6.55–8.05 (14H, m, 2OPh and 4CH_{arom}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 47.34 (d, $^1J_{PC} = 136.1$ Hz, P*C*HCH), 53.30 and 53.55 (2s, 2O*C*H$_3$), 54.51 (d, $^2J_{PC} = 3.0$ Hz, PCH*C*H), 112.33 (s, CH_{arom}), 120.28 and 120.56 (2d, $^3J_{PC} = 5.4$ Hz, 4C_{ortho}), 125.63 and 125.95 (2s, 2C_{para}), 126.11 (s, CH_{arom}), 129.83 and 130.12 (2s, 4C_{meta}), 139.48 (s, C_{arom}), 149.67 and 149.96 (2d, $^2J_{PC} = 8.9$ Hz, 2C_{ipso}), 151.09 (s, C_{arom}), 166.50 (d, $^2J_{PC} = 5.2$ Hz, CO), 170.08 (d, $^3J_{PC} = 6.7$ Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 11.04.

*Diethyl 2-(4-nitrophenylamino)-3-(diphenoxyphosphoryl)butandioate (***5d***)*

Yellow powder; yield: 92% (0.50 g), mp = 112–114°C. IR (KBr) (ν_{max}, cm^{-1}): 3368 and 3285 (2NH), 1730 and 1700 (C=O), 1265 (P=O). MS (*m/z*, %): 542 (M^+, 2), 404 (25), 331 (54), 285 (52), 255 (73), 138 (100), 108 (54), 65 (81). Anal. Calcd for $C_{26}H_{27}N_2O_9P$ (542.14): C, 57.57; H, 5.02; N, 5.16. Found: C, 57.43; H, 4.96; N, 5.22.

Major isomer (70%): ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 1.21 and 1.39 (6H, 2t, $^3J_{HH} = 7.1$ Hz, 2OCH$_2$C*H*$_3$), 4.17–4.31 (4H, m, 2OC*H*$_2$CH$_3$), 4.38 (1H, dd, $^3J_{HH} = 7.2$, $^2J_{PH} = 16.4$ Hz, PC*H*CH), 4.93 (1H, ddd, $^3J_{HH} = 3.6$, $^3J_{PH} = 7.6$, $^3J_{HH} = 10.7$ Hz, PCHC*H*), 5.75 (1H, d, $^3J_{HH} = 10.7$ Hz, N*H*), 6.57–8.08 (14H, m, 2OPh and 4CH_{arom}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 14.03 and 14.09 (2s, 2OCH$_2$*C*H$_3$), 47.10 (d, $^1J_{PC} = 137.8$ Hz, P*C*HCH), 54.41 (d, $^2J_{PC} = 3.5$ Hz, PCH*C*H), 62.50 and 62.85 (2s, 2 OC*H*$_2$CH$_3$), 112.79 (s, CH_{arom}), 120.21 and 120.57 (2d, $^3J_{PC} = 4.4$ Hz, 4C_{ortho}), 125.51 and 125.92 (2s, 2C_{para}), 126.06 (s, CH_{arom}), 129.71 and 129.98 (2s, 4C_{meta}), 139.46 (s, C_{arom}), 149.91 (d, $^2J_{PC} = 9.1$ Hz, C_{ipso}), 149.94 (d, $^2J_{PC} = 9.0$ Hz, C_{ipso}), 152.06 (s, C_{arom}), 167.54 (d, $^2J_{PC} = 5.3$ Hz, CO), 170.11 (d, $^3J_{PC} = 18.2$ Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 11.66.

Minor isomer (30%): ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 1.21 and 1.29 (6H, 2t, $^3J_{HH} = 7.1$ Hz, 2OCH$_2$C*H*$_3$), 4.23–4.43 (4H, m, 2OC*H*$_2$CH$_3$), 4.35 (1H, dd, $^3J_{HH} = 3.6$, $^2J_{PH} = 16.3$ Hz, PC*H*CH), 5.02 (1H, m, PCHC*H*), 5.46 (1H, d, $^3J_{HH} = 6.1$ Hz, N*H*), 6.57–8.08 (14H, m, 2OPh and 4CH_{arom}).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 13.95 and 14.03 (2s, 2 OCH$_2$*C*H$_3$), 47.51 (d, $^1J_{PC} = 137.7$ Hz, P*C*HCH), 54.68 (d, $^2J_{PC} = 3.5$ Hz, PCH*C*H), 62.67 and 62.75 (2s, 2OC*H*$_2$CH$_3$), 112.40 (s, CH_{arom}), 120.21 and 120.35 (2d, $^3J_{PC} = 4.6$ Hz, 4C_{ortho}), 125.61 and 125.85 (2s, 2C_{para}), 126.32 (s, CH_{arom}), 129.80 and 129.98 (2s, 4C_{meta}), 139.06 (s, C_{arom}), 149.68 (d, $^2J_{PC} = 8.3$ Hz, C_{ipso}), 149.79 (d, $^2J_{PC} = 8.7$ Hz, C_{ipso}), 151.25 (s, C_{arom}), 165.92 (d, $^2J_{PC} = 5.2$ Hz, CO), 169.55 (d, $^3J_{PC} = 7.2$ Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 11.41.

*Dimethyl 2-(2-amino-N-yl-benzoic acid)-3-(diphenoxyphosphoryl)butandioate (***5e***)*

Colorless crystalline; yield: 95% (0.49 g), mp = 152–154°C. IR (KBr) (ν_{max}, cm^{-1}): 3297 (NH), 1750 and 1730 (C=O), 12,890 (P=O). MS (*m/z*, %): 513 (M^+, 9), 453 (2), 421 (12), 376 (38), 137 (100), 77 (45). Anal. Calcd for $C_{25}H_{24}NO_9P$ (513.43): C, 58.48; H, 4.71; N, 2.73. Found: C, 58.56; H, 4.63; N, 2.67. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 3.75 and 3.90 (6H, 2s, 2OC*H*$_3$), 4.25 (1H, dd, $^3J_{HH} = 4.4$, $^2J_{PH} = 25.0$ Hz, PC*H*CH), 5.15 (1H, ddd, $^3J_{HH} = 4.4$, $^3J_{PH} = 9.5$, $^3J_{HH} = 10.4$ Hz, PC*H*CH), 6.70 (14H, m, Ar), 8.80 (1H, d, $^3J_{HH} = 10.4$ Hz, NH). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 47.32 (d, $^1J_{PC} = 137.3$ Hz, P*C*HCH), 53.03 and 53.21 (2s, 2O*C*H$_3$), 54.04 (s, PCH*C*H), 110.93, 112.62, 115.39, 116.63 (4s, $C_7H_6NO_2$), 120.34, (d, $^3J_{CP} = 4.4$ Hz, 2*C*H$_{ortho}$), 120.79 (d, $^3J_{CP} = 4.4$ Hz, 2*C*H$_{ortho}$), 125.24, 125.65 (2s, 2*C*$_{para}$), 129.48 and 129.87 (2s, 4*C*$_{meta}$), 132.48, 135.48 (2s, $C_7H_6NO_2$), 149.94 (d, $^2J_{CP} = 8.3$ Hz, C_{ipso}), 150.04 (d, $^2J_{CP} = 8.3$ Hz, C_{ipso}), 166.78 (d, $^2J_{PC} = 4.7$ Hz, CO), 171.25 (d, $^3J_{PC} = 16.2$ Hz, CO), 172.99 (s, CO_2H). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 11.76.

*Diethyl 2-(2-triflourophenylamino)-3-(diphenoxyphosphoryl)butandioate (***5f***)*

White powder; yield: 95% (0.51 g), mp = 92–93°C. IR (KBr) (ν_{max}, cm^{-1}): 3394 (NH), 1764 and 1734 (C=O), 1264 (P=O). MS (*m/z*, %): 537 (M^+, 83), 505 (21), 478 (100), 446 (35), 406 (9), 380 (13), 303 (26), 275 (31), 243 (10), 212 (16), 172 (20), 145 (13), 77 (49), 51 (13). Anal. Calcd for $C_{25}H_{23}F_3NO_7P$ (537.42): C, 55.87; H, 4.31; N, 2.61. Found: C, 55.82; H, 4.22; N, 2.69. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 3.73 and 3.90 (6H, 2s, 2OC*H*$_3$), 4.21 (1H, dd, $^3J_{HH} = 4.0$, $^2J_{PH} = 25.2$ Hz, PC*H*CH), 5.08 (1H, ddd, $^3J_{HH} = 4.0$, $^3J_{PH} = 9.1$ Hz, $^3J_{HH} = 10.5$ Hz, PC*H*CH), 5.89 (1H, d, $^3J_{HH} = 10.5$ Hz), 6.79–7.49 (14H, m, Ar). ^{13}C NMR (125.7 MHz, $CDCl_3$): δ_C 47.23 (d, $^1J_{PC} = 137.2$ Hz, P*C*HCH), 52.89 and 53.23 (2s, 2O*C*H$_3$), 54.96 (d, $^2J_{PC} = 3.0$ Hz, PCH*C*H), 115.14 (q, $^2J_{CF} = 32.0$ Hz, $C_7H_6F_3N$), 115.26, 117.82 (2s, $C_7H_6F_3N$), 120.37 (d, $^3J_{CP} = 4.0$ Hz, 2*C*H$_{ortho}$), 120.62 (d, $^3J_{CP} = 4.0$ Hz, 2*C*H$_{ortho}$), 124.82 (q, $^1J_{CF} = 272.6$ Hz, CF_3), 125.32 and 125.65 (2s, 2*C*$_{para}$), 126.58 (q, $^3J_{CF} = 5.5$ Hz,

$C_7H_6F_3N$), 129.47 and 129.82 (2s, 4C_{meta}), 133.00 (s, $C_7H_6F_3N$), 149.83(d, $^2J_{CP}$ = 9.6 Hz, C_{ipso}), 149.71 (d, $^2J_{CP}$ = 9.6 Hz, C_{ipso}), 155.96 (s, $C_7H_6F_3N$), 167.34 (d, $^2J_{PC}$ = 5.0 Hz, CO), 171.14 (d, $^3J_{PC}$ = 17.0 Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 11.72.

*Dimethyl 2-[1-(diphenylmethylene)hydrazine-N-yl]-3-(diphenoxyphosphoryl)butandioate (**5g**)*

Dark yellow viscous oil; yield: 93% (0.53 g), IR (in $CHCl_3$) (ν_{max}, cm^{-1}): 3317 (NH), 1746 and 1660 (C=O), 1277 (P=O). MS (*m/z*, %): 572 (M^+, 2), 392 (15), 326 (13), 223 (20), 196 (52), 105 (100), 77 (88), 51 (40). Anal. Calcd for $C_{31}H_{29}N_2O_7P$ (572.54): C, 65.03; H, 5.11; N, 4.89. Found: C, 64.97; H, 5.17; N, 4.81.

Major isomer (56%): ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 3.72 and 3.79 (6H, 2s, 2 OCH_3), 4.10 (1H, s, NH), 4.16 (1H, dd, $^3J_{HH}$ = 5.4, $^2J_{PH}$ = 24.7 Hz, PC*H*CH), 5.08 (1H, m, PCHC*H*), 6.77–7.84 (20H, m, 2OPh and 2Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 47.40 (d, $^1J_{PC}$ = 137.3 Hz, P*C*HCH), 52.71 and 53.03 (2s, 2O*C*H_3), 60.81 (d, $^2J_{PC}$ = 3.2 Hz, PCH*C*H), 120.51 and 120.58 (2d, $^3J_{PC}$ = 5.4 Hz, 4C_{ortho}), 125.32 and 125.66 (2s, 2C_{para}), 128.77 (s, 4CH_{arom}), 129.27 and 129.64 (2s, 4C_{meta}), 130.33 (s, C_{arom}), 131.43, 132.47, 138.05 and 148.92 (4s, 6CH_{arom} and 2C_{arom}), 150.07 and 150.21 (d, $^2J_{PC}$ = 9.4 Hz, C_{ipso}), 156.43 (s, C=N), 167.27 (d, $^2J_{PC}$ = 5.2 Hz, CO), 171.13 (d, $^3J_{PC}$ = 15.4 Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 11.62.

Minor isomer (44%): ^{1}H NMR (300.1 MHz, $CDCl_3$): δ_H 3.66 and 3.75 (6H, 2s, 2OCH_3), 4.03 (1H, s, NH), 4.46 (1H, dd, $^3J_{HH}$ = 8.9, $^2J_{PH}$ = 22.4 Hz, PC*H*CH), 4.91 (1H, dd, $^3J_{HH}$ = 8.9, $^2J_{PH}$ = 11.5 Hz, PCHC*H*), 6.77–7.84 (20H, m, 2OPh and 2Ph).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ_C 47.55 (d, $^1J_{PC}$ = 138.7 Hz, P*C*HCH), 52.79 and 53.40 (2s, 2O*C*H_3), 60.01 (d, $^2J_{PC}$ = 3.3 Hz, PCH*C*H), 120.14 and 120.75 (2d, $^3J_{PC}$ = 4.7 Hz, 4C_{ortho}), 125.27 and 125.50 (2s, 2C_{para}), 128.77 (s, 4CH_{arom}), 129.40 and 129.70 (2s, 4C_{meta}), 130.47 (s, C_{arom}), 131.45, 132.70, 138.41, and 147.68 (4s, 6CH_{arom} and 2C_{arom}), 150.00 and 150.14 (d, $^2J_{PC}$ = 7.4 Hz, C_{ipso}), 158.11 (s, C=N), 167.00 (d, $^2J_{PC}$ = 4.7 Hz, CO), 171.84 (d, $^3J_{PC}$ = 14.3 Hz, CO). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ_P 12.52.

*Dimethyl 2-(4,4-dimethyl-2,5-dioxoimidazolidin-1-yl)-3-(diphenoxyphosphoryl)butandioate (**7**)*

Yellow viscous oil; yield: 91% (0.46 g), IR (in CCl_4) (ν_{max} , cm^{-1}): 3068 (NH), 1748 and 1590 (C=O), 1204 (P=O). MS (*m/z*, %): 505 (M^+ +1, 1), 504 (M^+, 2), 473 (2), 411 (41), 377 (2), 326 (100), 285 (9), 128 (27), 94 (92), 77 (61). Anal. Calcd for $C_{23}H_{25}N_2O_9P$ (504.43): C, 54.76; H, 5.00; N, 5.55. Found: C, 54.87; H, 4.93; N, 5.62.

Major isomer (67%): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.35 and 1.37 (6H, 2s, 2CH_3), 3.76 and 3.86 (6H, 2s, 2OCH_3), 4.53 (1H, dd, $^3J_{HH}$ = 11.5, $^2J_{PH}$ = 21.2 Hz, PC*H*CH), 5.70 (1H, dd, $^3J_{HH}$ = 11.5, $^3J_{PH}$ = 5.3 Hz, PCHC*H*), 6.63–7.32 (10H, m, 2 OPh), 9.31 (1H, s, N*H*).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 24.40 and 24.70 (2s, 2*C*H_3), 40.69 (d, $^1J_{PC}$ = 134.4 Hz, P*C*HCH), 43.97 (d, $^2J_{PC}$ = 4.5 Hz, PCH*C*H), 53.28 and 53.60 (2s, 2O*C*H_3), 60.34 (s, *C*Me_2), 120.13 (d, $^3J_{PC}$ = 4.8 Hz, 2C_{ortho}), 120.19 (d, $^3J_{PC}$ = 4.9 Hz, 2C_{ortho}), 123.75 (s, 2C_{para}), 129.42 and 129.67 (2s, 4C_{meta}), 149.47 (d, $^2J_{PC}$ = 7.2 Hz, C_{ipso}), 149.58 (d, $^2J_{PC}$ = 7.5 Hz, C_{ipso}), 152.45 (CMe_2*C*O), 156.66 (N*C*ON), 166.65 (d, $^2J_{PC}$ = 7.6 Hz, CO), 168.12 (d, $^3J_{PC}$ = 18.9 Hz, CO). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ_P 10.23.

Minor isomer (33%): ^{1}H NMR (400.1 MHz, $CDCl_3$): δ_H 1.35 and 1.37 (6H, 2s, 2CH_3), 3.74 and 3.86 (6H, 2s, 2OCH_3), 4.34 (1H, dd, $^3J_{HH}$ = 3.1, $^2J_{PH}$ = 9.1 Hz, PC*H*CH), 5.62 (1H, br s, PCHC*H*), 6.63–7.32 (10H, m, 2OPh), 9.03 (1H, s, N*H*).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C 24.40 and 24.70 (2s, 2*C*H_3), 40.69 (d, $^1J_{PC}$ = 134.4 Hz, P*C*HCH), 43.97 (d, $^2J_{PC}$ = 4.5 Hz, PCH*C*H), 53.26 and 53.53 (2s, 2O*C*H_3), 59.35 (s, *C*Me_2), 120.42 (d, $^3J_{PC}$ = 4.7 Hz, 2C_{ortho}), 120.60 (d, $^3J_{PC}$ = 4.5 Hz, 2C_{ortho}), 125.67 (s, 2C_{para}), 129.84 and 129.88 (2s, 4C_{meta}), 149.94 (d, $^2J_{PC}$ = 7.2 Hz, C_{ipso}), 150.40 (d, $^2J_{PC}$ = 7.5 Hz, C_{ipso}), 152.53 (CMe_2*C*O), 156.74 (N*C*ON), 166.60 (d, $^2J_{PC}$ = 6.6 Hz, CO), 168.06 (d, $^3J_{PC}$ = 18.5 Hz, CO). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ 11.63.

Crystal Structure Determination

Crystallographic data for the structure were collected at 100(2) K on an Oxford Diffraction (Oxfordshire, UK) Xcalibur diffractometer fitted with graphite-monochromated Mo Kα radiation. Following multi-scan absorption corrections and solution by direct methods, the structure was refined against F^2 with full-matrix least squares using the program SHELXL-97 [41]. The hydroxyl hydrogen atom H(311) was allowed to refine without restraints. All other H-atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms.

Crystal Data

$C_{25}H_{24}NO_9P$, M = 513.42, monoclinic, space group $P2_1/n$, a = 8.8905(3), b = 20.7227(7), c = 13.8954(5)

Å, $\beta = 105.083(4)^\circ$, $V = 2471.83(15)$ Å^3, $Z = 4$, $\mu = 0.166$ mm^{-1}, 23,047 reflections collected, 6739 unique ($R_{int} = 0.0652$). Final R indices $R_1 = 0.0526$, $wR_2 = 0.0952$ [$I > 2\sigma I$)]; $R_1 = 0.1238$, $wR_2 = 0.1104$ (all data). CCDC deposition code: 798758.

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