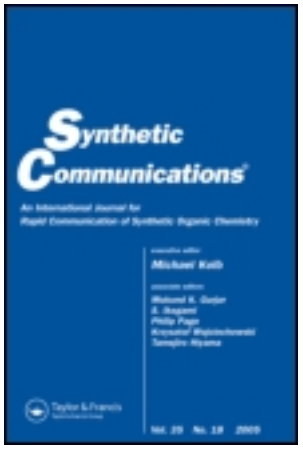

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Synthesis of Dialkyl 2-(Dialkoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl Sulfanyl) Succinates

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SYNTHESIS OF DIALKYL 2-(DIALKOXYPHOSPHORYL)-3-(4-OXO-4,5-DIHYDRO-THIAZOLE-2-YL SULFANYL) SUCCINATES

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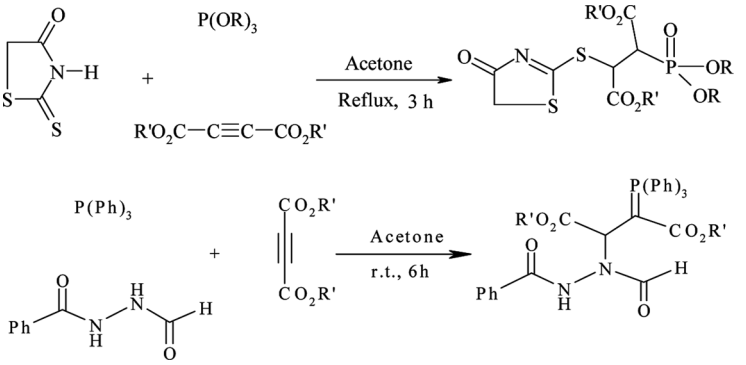
GRAPHICAL ABSTRACT



Abstract *A three-component reaction of trialkyl(aryl) phosphites, dialkyl acetylenedicarboxylates and rhodanine is described as a simple and efficient route for synthesis of dialkyl 2-(dialkoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl) succinates in good yields. Protonation of the reactive 1:1 intermediate produced in the reaction between dialkyl acetylenedicarboxylate and triphenylphosphine by* N′*-formylbenzohydrazide leads to vinylphosphonium salts, which undergo Michael addition with the conjugate base of the NH acid to produce highly functionalized, salt-free phosphorus ylides in excellent yields.*

Keywords Dialkyl acetylenedicarboxylates; NH acids; phosphorus ylides; trialkyl(aryl) phosphites; triphenylphosphine

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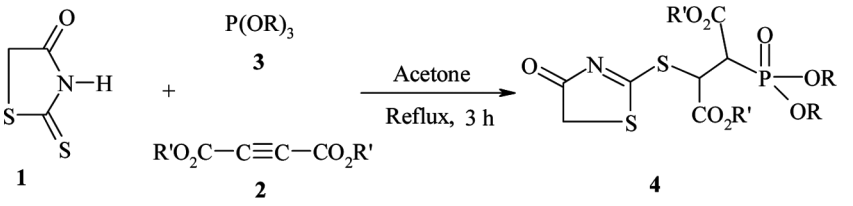
INTRODUCTION

Organophosphonates have been used as substitutes for the corresponding esters and acids with high biological activity.[1,2] As a result, a large number of methods have appeared describing novel syntheses of organophosphorus compounds. The attack by nucleophilic trivalent phosphorus on a carbon atom is facilitated when the latter is part of, or conjugated with, a carbonyl group or when it is part of an unsaturated bond otherwise activated.[3–9] The reaction of trimethyl phosphite and dimethyl acetylenedicarboxylate (DMAD) in the presence of alcohols is reported to produce phosphite ylide derivatives, which are stable at low temperatures but are converted to phosphonate derivatives warming or by treatment with water.[10] There are some other recent reports on the reaction between phosphites and acetylenic esters in the presence of an acidic organic compound, all of them proceeding through a phosphite ylide intermediate.[11–24] In continuation of our previous works on the reaction of trivalent phosphorus nucleophiles and acetylenic esters in the presence of organic NH, OH, or CHacids,[19–25] here we report the results of our study on the reaction between dialkyl acetylenedicarboxylates (DAADs) and trialkyl(aryl) phosphites in the presence of rhodanine.

The reaction of DAAD **2** with trialkyl(aryl) phosphite **3** in the presence of rhodanine **1** leads to dialkyl 2-(dialkoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl) succinates **4** in good yields (Scheme 1).

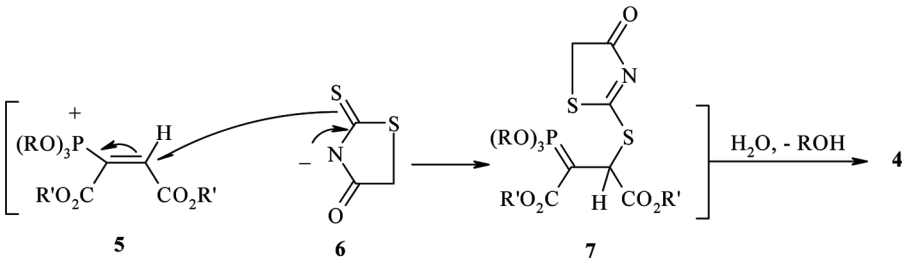
Products **4a–e** were all new compounds, and their structures were deduced from their elemental analyses and spectral data. The mass spectrum of compound **4a** showed the molecular ion peak at 385. The ^{1}H NMR spectrum of compound **4a** displayed two doublets ($J_{HP} = 11$ Hz) at 3.71 and 3.76 ppm for two $POCH_3$



4	R	R'	Yield*
a	Me	Me	91
b	Et	Me	89
c	Bu	Me	87
d	Me	Et	90
e	Ph	Me	90

* Isolated yields

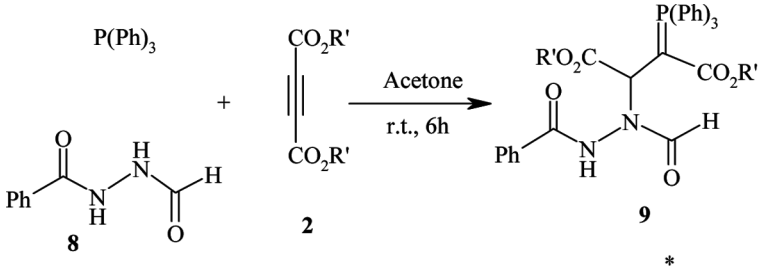
Scheme 1. Synthesis of dialkyl 2-(dialkoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl) succinates by reaction of DAAD and trialkyl(aryl) phosphites in the presence of rhodanine.



Scheme 2. Suggested mechanism for formation of compound **4**.

groups and two singlets at 3.70 and 3.81 ppm for two methoxycarbonyl groups. Two signals were absorbed at 4.32 (dd, $^{3}J_{HH} = 11$ Hz, $^{2}J_{HP} = 21$ Hz) and 4.54 ppm (dd, $^{3}J_{HH} = 11$ Hz, $^{3}J_{HP} = 5$ Hz) for two vicinal methine protons. One signal was absorbed at 3.68 for two methylene protons. The ^{13}C NMR spectrum of compound **4a** showed 11 distinct resonances in agreement with the proposed structure. The structural assignments made on the basis of the NMR spectra of compound **4a** were supported by its infared (IR) spectrum; the ester carbonyl groups exhibited strong absorption bands at 1736 and 1700 cm^{-1}. The ^{31}P NMR spectrum of compound **4a** displays a signal at 19.22 ppm.

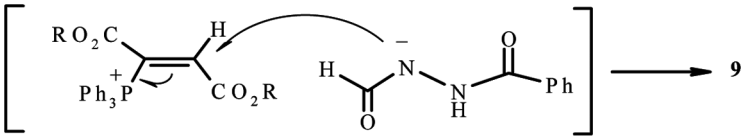
A reasonable mechanism for the formation of compound **4** is presented in Scheme 2. The initial addition of trialkyl(aryl) phosphite on DAAD leads to a diionic intermediate that is protonated by rhodanine to produce the vinyl phosphonium **5**. It is well known that thioamide usually undergoes nucleophilic addition from the sulfur atom, because sulfur is more nucleophilic than the nitrogen atom. Also in the ^{13}CNMR spectrum of compound **4** we do not observe any signal at magnetic fields lower than 172 ppm, and the C=S carbon is expected to be observed at about



9	R'	%Yield*
a	CH_3	93
b	C_2H_5	91
c	t-Bu	93

* Isolated yields

Scheme 3. Three-component reaction of triphenylphosphine, dialkyl acetylenedicarboxylate, and N′-formylbenzohydrazide.



Scheme 4. Suggested mechanism for formation of compound **9**.

195 ppm. So, we can conclude that compound **4** is formed by the conjugate addition of anion **6** from the sulfur atom on phosphonium cation **5**, which afforded the phosphite ylide **7**, which then hydrolyzed to product **4**.

The reaction of acetylenic ester **2** with triphenylphosphine in the presence of *N*′-formylbenzohydrazide **8** leads to functionalized phosphoranes **9** in excellent yields (Scheme 3).

The ^{1}H NMR spectrum of **9a** exhibits two sharp lines at $\delta = 3.03$ and 3.76 ppm for the protons of two methoxy groups and a doubled signal for the methine proton at 4.96 ppm ($^{3}J_{HP} = 16$ Hz). One single signal is absorbed at 9.05 ppm, and disappeared after addition of a few drops of D_2O to solution of compound **9a**. This signal is related to the NH proton. Aromatic protons resonate between 7.37 and 7.96 ppm as multiplets and a single signal at 8.35 ppm for the CH=O proton. ^{13}C NMR spectra of compound **9a** shows 16 distinct signals, which is consistent with the proposed structure. The ^{31}P NMR spectrum of compound **9a** consists of one signal at 24.37. This shift is similar to those absorbed for other stable phosphorus ylides.[26,27] The structural assignments made on the basis of the NMR spectra of compounds **9a–c** are supported by their IR spectra. The carbonyl groups exhibited strong absorption bands at 1717, 1691, and 1618 cm^{-1} and showed the stretching absorption bond related to NH bond.

It is reasonable to assume that ylide **9** results from the initial addition of triphenylphosphine to DAAD and subsequent protonation of the 1:1 adduct by the NH-acidic *N*′-formylbenzohydrazide. The positively charged ion **10** is then attacked by anion **11** to form the phosphorane **9** (Scheme 4).

In summary, we report herein that the three-component reaction of trialkyl-(aryl) phosphites, dialkyl acetylenedicarboxylates, and rhodanine provides a simple and efficient one-pot route for the synthesis of dialkyl 2-(dialkoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl)succinates in good yields, and the reaction between dialkyl acetylenedicarboxylate and triphenylphosphine by *N*′-formylbenzohydrazide produces highly functionalized, salt-free phosphorus ylides in excellent yields.

EXPERIMENTAL

Melting points were determined with an Electrothermal 9100 apparatus. Elemental analyses were performed at the analytical laboratory of the Science and Researches Unit of Islamic Azad University. Mass spectra were recorded on a Finnigan-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H, ^{13}C, and

^{31}P NMR spectra were recorded on a Bruker DRX-500 Avance spectrometer in $CDCl_3$ and dimethylsulfoxide (d_6-DMSO) using tetramethylsilane (TMS) as internal standard or 85% H_3PO_4 as external standard. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

Compounds 4a–e

General procedure. A mixture of dialkyl acetylenedicarboxylate (2 mmol) in acetone (3 mL) was added dropwise at room temperature to a magnetically stirred solution of trialkyl(aryl) phosphite (2 mmol) and rhodanine (2 mmol) in acetone (15 mL) over 2 min. The reaction mixture was then stirred for 3 h at reflux temperature. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (60, 230–400 mesh) using ethyl acetate–hexane (2:1) mixture as eluent.

Dimethyl 2-(dimethoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl) succinate (4a). Yield: 91%; yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 1736, (C=O, ester), 1700 (C=O, amide), Analyses: calcd. for $C_{11}H_{16}NO_8PS_2$: C, 34.28; H, 4.19; N, 3.63%. Found: C, 34.2; H, 4.15; N, 3.7%. MS (m/z, %): 385 (M^+, 3), 353 (M $^-CH_3OH$, 65), 109 [$(CH_3O)_2P$=O, 80], 294 (353 $^-CO_2CH_3$, 100). ^1H NMR (500 M Hz, $CDCl_3$): δ 3.68 (2H, s, CH_2), 3.70 and 3.81 (6 H, 2 s, 2 OCH_3), 3.71 and 3.76 (6 H, d $^3J_{PH} = 11$ Hz, 2$POCH_3$), 4.32 (1 H, dd, $^2J_{HP} = 21$ Hz, $^3J_{HH} = 12$ Hz, P-*C*H), 4.54 (1 H, dd, $^3J_{HP} = 5$ Hz, $^3J_{HH} = 12$ Hz, P-C-CH). ^{13}C NMR (125.8 M Hz, $CDCl_3$): δ 40.20 (d, $^1J_{cp} = 137$ Hz, P-*C*), 45.08 (CH_2), 53.89 (m, CH), 54.38 (m, 2 PO*C*H_3), 53.64 and 53.68 (2 OCH_3), 156.2 (SC=N), 167.43 (d, $^2J_{CP} = 7$ Hz, C=O), 167.86 (C=O), 172.88 (d, $^3J_{CP} = 21$ Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.22.

Dimethyl 2-(diethoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl) succinate (4b). Yield: 89%; yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 1732, (C=O, ester), 1700 (C=O, amide). Analyses: calcd. for $C_{13}H_{20}NO_8PS_2$: C, 37.77; H, 4.88; N, 3.39%. Found: C, 37.9; H, 5.00; N, 3.3%. MS (m/z, %): 413 (M^+, 8), 381 (M $^-CH_3OH$, 55), 137 [$(EtO)_2P$=O, 74], 322 (381 $^-CO_2CH_3$, 100). ^1H NMR (500 M Hz, $CDCl_3$): δ 1.23 and 1.30 (6 H, 2 t $^3J_{HH} = 7$ Hz, 2 CH_3), 3.64 (2 H, s, CH_2), 3.76 and 3.98 (6 H, 2 s, 2 OCH_3), 4.00 –4.13 (5H, m, 2 OCH_2 and CH), 4.32 (1 H, dd, $^3J_{HH} = 11$ Hz, $^3J_{HP} = 4$ Hz, CH). ^{13}C NMR (125.8 M Hz, $CDCl_3$): δ 16.52 and 16.61 (2 CH_3), 42.38 (d, $^1J_{cp} = 132$ Hz, P-*C*), 45.03 (CH_2), 53.38 and 53.41 (2 OCH_3), 53.80 (d, $^2J_{CP} = 3$ Hz, CH), 63.51–63.93 (m, 2 PO*C*H_2), 156.5 (SC=N), 167.87 (C=O), 167.56 (d, $^2J_{CP} = 7$ Hz, C=O), 171.95 (d, $^3J_{CP} = 21$ Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.35.

Dimethyl 2-(dibutoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl) succinate (4c). Yield: 87%; yellow oil. IR (KBr) (ν_{max} cm^{-1}): 1739, (C=O, ester), 1701 (C=O, amide). Analyses: calcd. for $C_{17}H_{28}NO_8PS_2$: C, 43.49; H, 6.01; N, 2.98%. Found: C, 43.4; H, 6.1, N, 3.00%. MS (m/z, %): 469 (M^+, 6), 433 (M $^-CH_3OH$, 62), 193 [$(n\text{-}BuO)_2P$=O, 48], 374 (433 $^-CO_2CH_3$, 100).^1H NMR (500 MHz, d_6-DMSO-Me_4Si): δ 0.82, and 0.86 (6 H, 2 t, 2 CH_3), 1.32 (4 H, m, 2

CH_2), 1.56 (4 H, m, 2 CH_2), 3.64 (2 H, s, CH_2), 3.68 and 3.74 (6 H, 2 s, 2 OCH_3), 3.94–4.04 (4 H, m, 2 OCH_2), 4.22 (1 H, dd, $^3J_{HP} = 6$ Hz, $^3J_{HH} = 11$ Hz, CH), 4.36 (1 H, dd, $^2J_{HP} = 21$ Hz, $^3J_{HH} = 12$ Hz, P-*C*H). ^{13}C NMR (125.8 MHz, d_6-DMSO-Me_4Si): δ 13.89 and 13.91 (2 *C*H_3), 18.92 and 18.99 (2 CH_2), 32.64 and 32.74 (2d, $^3J_{CP} = 7$ Hz, 2 CH_2), 45.01 (d, $^1J_{cp} = 127$ Hz, P-*C*), 45.19 (CH_2), 53.78 (d, $^2J_{cp} = 4$ Hz, P-C-*C*), 53.15 and 53.31 (2 O*C*H_3), 66.85–67.54 (m, 2 PO*C*H_2), 156.2 (SC=N), 167.51 (d, $^2J_{CP} = 7$ Hz, C=O), 167.94 (C=O), 171.85 (d, $^3J_{CP} = 21$ Hz, Hz, C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 19.24.

Diethyl 2-(dimethoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl) succinate (4d). Yield: 90%; yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 1742, (C=O, ester), 1712 (C=O, amide); Analyses: calcd. for $C_{13}H_{20}NO_8PS_2$: C, 37.77; H, 4.88; N, 3.39%. Found: C, 37.9; H, 5.00; N, 3.3%. MS (*m*/*z*, %): 413 (M^+, 3), 367 (M $^-C_2H_5OH$, 58), 109 [$(CH_3O)_2P$=O, 68], 294 (367 $^-CO_2C_2H_5$, 100).^{1}H NMR (500 MHZ, $CDCl_3$): δ 1.18 and 1.28 (6 H, 2 t $^3J_{HH} = 7$ Hz, 2 CH_3), 3.62 (2 H, s, CH_2), 3.71–3.78 (6 H, m, 2 POC*H*$_3$), 4.12–4.27 (4 H, m, 2 OCH_2), 4.55 (1 H, dd, $^2J_{HP} = 21$ Hz, $^3J_{HH} = 12$ Hz, P-*C*H), 4.68 (1 H, dd, $^3J_{HP} = 5$ Hz, $^3J_{HH} = 12$ Hz, P-C-CH).^{13}C NMR (125.8 M Hz, $CDCl_3$): δ 14.26 and 14.42 (2 CH_3), 45.12 (CH_2), 48.46 (d, $^1J_{cp} = 137$ Hz, P-*C*), 53.58 (d, $^2J_{CP} = 3$ Hz, CH), 54.32 (m, 2 PO*C*H_3), 62.50 and 62.18 (2 O*C*H_2), 153.8 (SC=N), 166.97 (d, $^2J_{CP} = 7$ H_Z, C=O), 167.25 (C=O), 172.43 (d, $^3J_{CP} = 21$ Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.28.

Dimethyl 2-(diphenoxyphosphoryl)-3-(4-oxo-4,5-dihydro-thiazole-2-yl sulfanyl) succinate (4e). Yield: 90%; Yellow oil. IR (KBr) (ν_{max}, cm^{-1}): 1739, (C=O, ester), 1706 (C=O, amide). Analyses: calcd. for $C_{21}H_{20}NO_8PS_2$: C, 49.51; H, 3.96; N, 2.75%. Found: C, 49.6; H, 3.8; N, 2.7%. MS (*m*/*z*, %): 509 (M^+, 7), 477 (M $^-CH_3OH$, 35), 233 [$(PhO)_2P$=O, 100], 418 (477 $^-CO_2CH_3$, 100). ^{1}H NMR (500 M Hz, $CDCl_3$): δ 3.71 (2 H, s, CH_2), 3.89 and 3.99 (6 H, 2 s, 2 OCH_3), 4.32 (1 H, dd, $^3J_{HP} = 5$ Hz, $^3J_{HH} = 12$ Hz, P-C-CH), 4.53(1 H, dd, $^2J_{HP} = 21$ Hz, $^3J_{HH} = 12$ Hz, P-*C*H), 7.13–7.34 (10 H, m, 10 CH aromatic). ^{13}C NMR (125.8 M Hz, $CDCl_3$): δ 45.08 (CH_2), 45.57 (d, $^1J_{cp} = 137$ Hz, P-*C*), 53.47 (d, $^2J_{CP} = 3$ Hz, CH), 53.78 and 53.85 (2 OCH_3), 120.77 (d, $^3J_{CP} = 5$ Hz, 4 CH_{ortho}), 126.04 (s, 2 CH_{para}), 130.24 (d, $^4J_{cp} = 8$ Hz, 4 CH_{meta}), 150.33 (d, $^2J_{cp} = 10$ Hz, C_{ipso}), 150.44 (d, $^2J_{cp} = 10$ Hz, C_{ipso}), 156.03 (SC=N), 166.71 (d, $^2J_{CP} = 7$ Hz, C=O), 167.45 (C=O), 171.08 (d, $^3J_{CP} = 21$ Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 19.33.

Compounds 9a–c

General procedure. DAAD (2 mmol) in 10 mL acetone was added to a magnetically stirred solution of N′-[2-(phenyl)-acetyl]-formic acid hydrazide (2 mmol) and triphenylphosphine (2 mmol) in acetone (15 mL) at room temperature over 2 min. The reaction mixture was then allowed to stir for 6 h. The solvent was evaporated at reduced pressure. The residue was precipitated in a solution of diethyl ether–hexane. The solid was filtered and washed with diethyl ether to give the pure product.

Compound 9a. White powder; mp 171–173 °C. IR (KBr) (ν_{max}, cm^{-1}): 3365 (NH), 1717, 1691, 1618 (C=O). Analyses: calcd. for $C_{32}H_{29}N_2O_6P$: C, 67.60; H, 5.14;

N, 4.93%. Found: C, 67.8; H, 5.3; N, 4.8%. MS (m/z, %): 568 (M^+, 3), 105 (COPh, 80), 262 (PPh_3, 85), 77 (Ph, 100).^{1}H NMR (500 MHz, d_6-DMSO): δ 3.03 (3H, s, OCH_3), 3.76 (3H, s, OCH_3), 4.98 (1H, d, $^3J_{PH} = 16$ Hz), 7.37–7.96 (20H, m, aromatic), 8.35 (1H, s, CH=O), 9.05 (1H, s, NH). ^{13}C NMR (125.8 MHz, d_6-DMSO): δ 40.67 (d, $^1J_{PC} = 128$ Hz, C=P), 49.91, 53.16 (2 OCH_3), 58.91 (d, $^2J_{PC} = 17$ Hz, CH), 126.2 (d, $^1J_{PC} = 91$ Hz), 129.15 (d, $^2J_{PC} = 12$ Hz), 132.68 (d, $^4J_{PC} = 2$ Hz), 134.14 (d, $^3J_{PC} = 10$ Hz), 128.31, 129.0, 132.26 and 132.88 (ph), 164.38, 168.42 (2C=O), 168.6 (d, $^2J_{PC} = 12$ Hz C=O), 172.44 (d, $^3J_{PC} = 12$ Hz C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 24.37.

Compound 9b. White powder; mp 157–159 °C. IR (KBr) (ν_{max}, cm^{-1}): 3425 (NH), 1762, 1690, 1619 (C=O). Analyses: calcd. for $C_{34}H_{33}N_2O_6P$: C, 68.45; H, 5.58; N, 4.70%. Found: C, 68.3; H, 5.7; N, 4.9%. MS (m/z, %): 568 (M^+, 7), 105 (COPh, 100), 262 (PPh_3, 74), 77 (Ph, 95).^{1}H NMR (500 MHz, d_6-DMSO): δ 0.35 (3H, d $^3J_{HH} = 7$ Hz, CH_3), 1.32 (3H, d $^3J_{HH} = 7$ Hz, CH_3), 3.51–3.61 (2H, m, OCH_2), 4.13–4.32 (2H, m, OCH_2), 4.99 (1H, d, $^3J_{PH} = 16$ Hz), 7.37–7.98 (20H, m, aromatic), 8.22 (1H, s, CH=O), 8.97 (1H, s, NH). ^{13}C NMR (125.8 MHz, d_6-DMSO): δ 14.34 and 14.74 ($2CH_3$), 40.50 (d, $^1J_{PC} = 128$ Hz, C=P), 58.51, 61.99 ($2OCH_2$), 58.89 (d, $^2J_{PC} = 17$ Hz, CH), 126.49 (d, $^1J_{PC} = 91$ Hz), 129.04 (d, $^2J_{PC} = 12$ Hz), 132.60 (d, $^4J_{PC} = 2$ Hz), 134.21 (d, $^3J_{PC} = 10$ Hz), 128.34, 129.2, 132.36 and 132.71 (ph),164.37,168.40 (2C=O), 171.55 (d, $^2J_{PC} = 12$ Hz C=O), 171.77 (d, $^3J_{PC} = 12$ Hz C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 24.12.

Compound 9c. White powder; m.p. 180–182 °C. IR (KBr) (ν_{max}, cm^{-1}): 3410 (NH), 1730, 1697, 1613 (C=O). Analyses: calcd. for $C_{38}H_{41}N_2O_6P$: C, 69.92; H, 6.33; N, 4.29%. Found: C, 70.1; H, 6.5; N, 4.4%. MS (m/z, %): 652 (M^+, 15), 105 (COPh, 84), 262 (PPh_3, 70), 77 (Ph, 100).^{1}H NMR (500 MHz, d_6-DMSO): δ 0.79 (9H, s, $3CH_3$), 1.54 (9H, s, $3CH_3$), 4.86 (1H, d, $^3J_{PH} = 16$ Hz,), 7.33-8.03 (20H, m, aromatic), 8.23 (1H, s, CH=O), 9.05 (1H, s, NH). ^{13}C NMR (125.8 MHz, d_6-DMSO): δ 28.65 and 28.67 ($6CH_3$), 40.10 (d, $^1J_{PC} = 128$ Hz, C=P), 59.58 (d, $^2J_{PC} = 17$ Hz, CH), 78.29 and 81.80 (2C), 127.08 (d, $^1J_{PC} = 91$ Hz), 128.88 (d, $^2J_{PC} = 12$ Hz), 132.47 (d, $^4J_{PC} = 2$ Hz), 134.24 (d, $^3J_{PC} = 10$ Hz), 128.56, 129.0, 132.33 and 132.63 (ph), 164.27, 168.27 (2C=O), 170.65 (d, $^2J_{PC} = 12$ Hz C=O), 171.38 (d, $^3J_{PC} = 12$HZ C=O). ^{31}P NMR (202.5 MHz, d_6-DMSO): δ 23.94.

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