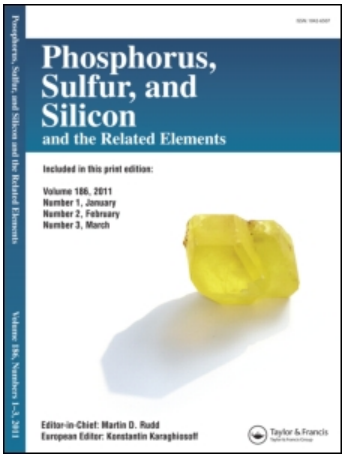

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A Simple Synthesis of Stable Phosphorus Ylides Derived from 2-Benzoxazolinone and 2-Mercaptobenzoxazole

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A Simple Synthesis of Stable Phosphorus Ylides Derived from 2-Benzoxazolinone and 2-Mercaptobenzoxazole

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The reaction of triphenylphosphine with dialkyl acetylenedicarboxylates in the presence of a strong SH-acid or NH-acid, such as 2-mercaptobenzoxazole and 2-benzoxazolinone, has been studied. In some cases, stable phosphorus ylides are obtained in excellent yields. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group, and the rotation about the partial double bond in (E) and (Z) geometrical isomers is slow on the NMR time scale at an ambient temperature. Thus, these exist as a mixture of geometrical isomers.

Keywords Acetylenic ester; dialkyl acetylenedicarboxylates; NH-acid; SH-acid; stable phosphorus ylides; triphenylphosphine

INTRODUCTION

Phosphorus ylides are reactive systems, which take part in many reactions of value in organic synthesis.[1–11] These ylides are usually prepared by the treatment of phosphonium salt with a base, and phosphonium salts are usually prepared from the phosphine and an alkyl halide.[1–5] Phosphonium salts are also prepared by a Michael addition of phosphorus nucleophiles to activated olefins, among other methods.[1,2] We wish to describe here an efficient synthetic route to 2-mercaptobenzoxazole and 2-benzoxazolinone–containing stable phosphorus ylides. Thus, the reaction of triphenylphosphine with dialkyl acetylenedicarboxylates **1** in the presence of strong NH-acid **2** leads

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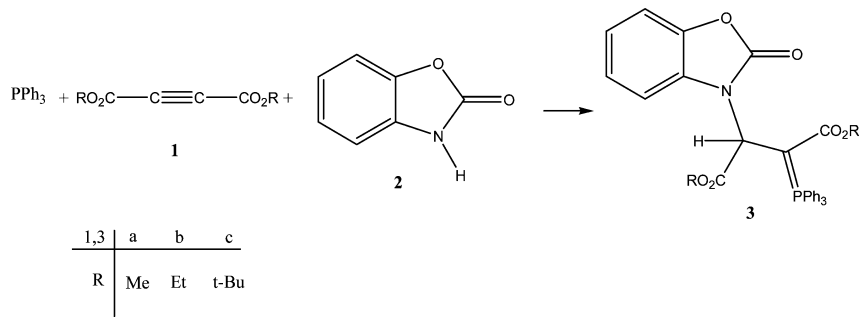


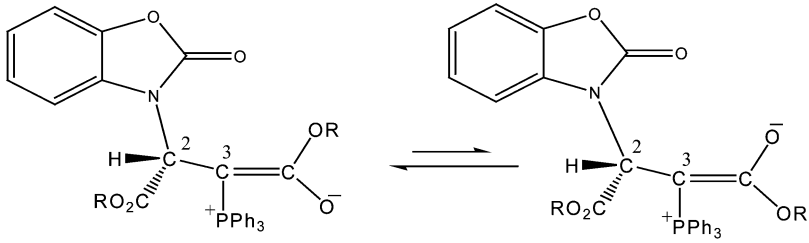
SCHEME 1

to the corresponding stable phosphorus ylides **3** in excellent yields (Scheme 1).

RESULTS AND DISCUSSION

The reaction of 2-benzoxazolinone with dialkyl acetylenedicarboxylates **1** in the presence of triphenylphosphine proceeded at r.t. in ethyl acetate and was finished after 24 h. ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of phosphorane **3**. Any product other than **3** could not be detected by NMR spectroscopy. The structures of compounds **3a–c** were deducted from their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. Mass spectra of these stable ylides displayed molecular ion peaks at appropriate m/z values. Any initial fragmentation involved a loss from or complete loss of the side chains and a scission of the hetrocyclic ring system.

^{1}H, ^{13}C, and ^{31}PNMR spectra of ylides **3a–c** are consistent with the presence of two isomers. The ylides moiety of these compounds is strongly conjugated with the adjacent carbonyl group, and the rotation about the partial double bond in 3-(E) and 3-(Z) geometrical isomers (Scheme 2) is slow on the NMR time scale at an ambient temperature.



SCHEME 2

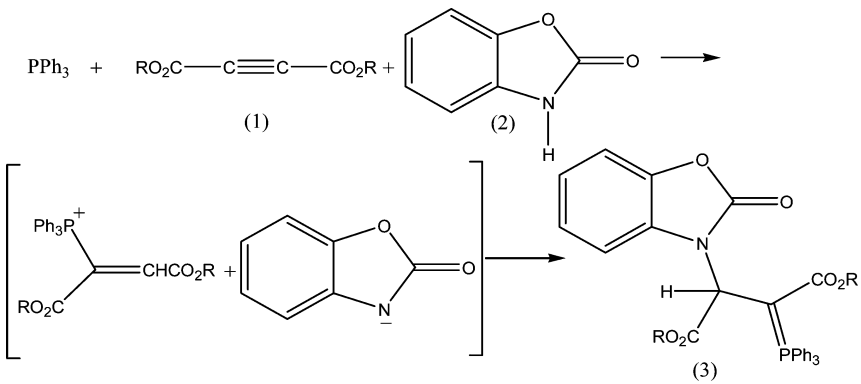
TABLE I Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-2, OR, CO_2R, C-2, and C-3 in the Major (M) and Minor (m) Diastereoisomers of Compounds 3a–c

Compound	Isomer (%)	^{1}H NMR Data			^{13}C NMR Data		
		H-2($^{3}J_{PH}$)	OR	CO_2R	C-2($^{2}J_{PC}$)	C-3($^{1}J_{PC}$)	^{31}P NMR
3a	M(72)	5.12 (16.40)	3.19	3.80	57.79 (16.51)	40.11 (124.75)	23.71
3a	m(28)	5.04 (18.48)	3.70	3.79	57.93 (17.93)	40.46 (134.47)	24.43
3b	M(75)	5.10 (16.96)	3.75	4.22	57.86 (16.61)	39.88 (124.31)	23.72
3b	m(25)	4.99 (21.19)	3.78	4.26	58.00 (19.92)	40.23 (132.98)	24.81
3c	M	4.95 (17.77)	1.02	1.59	58.34 (16.66)	39.32 (124.55)	23.30

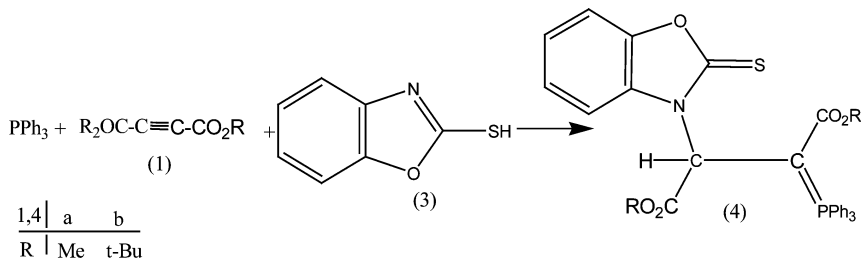
Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **3a–c** are shown in Table I. Assignment of configuration (Z) to the minor geometrical isomer is based on the ^{1}H chemical shift of the OR moiety, which is expected to be shielded as a result of the anisotropic effect of the phenyl groups.

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles,[10–14] it is reasonable to assume that phosphorus ylide **3** results from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the N-H acid **2**. Then the positively charged ion is attacked by the nitrogen atom of the conjugate base of the NH-acid to from phosphorane **3** (Scheme 3).

The reaction of triphenylphosphine with dialkyl acetylenedicarboxylates **1** in the presence of strong SH-acids **3** leads to the corresponding stable heterocyclic phosphorus ylides **4** in excellent yields (Scheme 4).



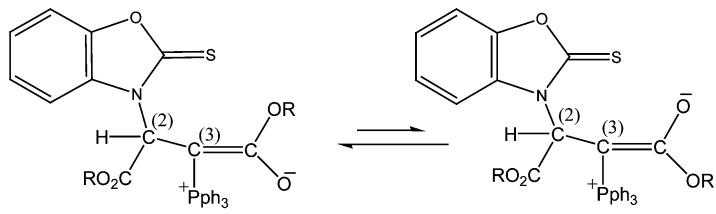
SCHEME 3



SCHEME 4

The reaction of 2-mercaptobenzoxazole **3** with dialkyl acetylenedicarboxylates **1** in the presence of triphenylphosphine proceeded at r.t. in acetone and was finished within a few hours. ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **4**. Structures of compounds **4a–b** were deducted from their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The ^{13}C NMR spectrum of compound **4a** exhibited a signal at 180.09 ppm for the C=S moiety.[14] The mass of these stable ylides displayed molecular ion peak at appropriate m/z values. Any initial fragmentation involved a loss of the side chains and scission of the heterocyclic ring system.^{1}H, ^{13}C, and ^{31}P NMR spectra of ylides **4a** were consistent with the presence of two isomers. The ylide moiety of these compounds was strongly conjugated with the adjacent carbonyl group, and rotation about the partial double bond in (E)-3 and (Z)-3 geometrical isomers (Scheme 5) was slow on the NMR timescale at an ambient temperature. Selected ^{1}H, ^{13}C, and ^{31}P NMR chemical shifts and coupling constants in the major (M) and minor (m) geometrical isomers of compounds **4a** are shown in Table II. Only one geometrical isomer was observed for di-tert-butyl derivatives of **4** presumably because of the bulky tert-butyl groups.

On the basis of the well-established chemistry of trivalent phosphorus nocleophiles,[10–14] it is reasonable to assume that phosphorus



SCHEME 5

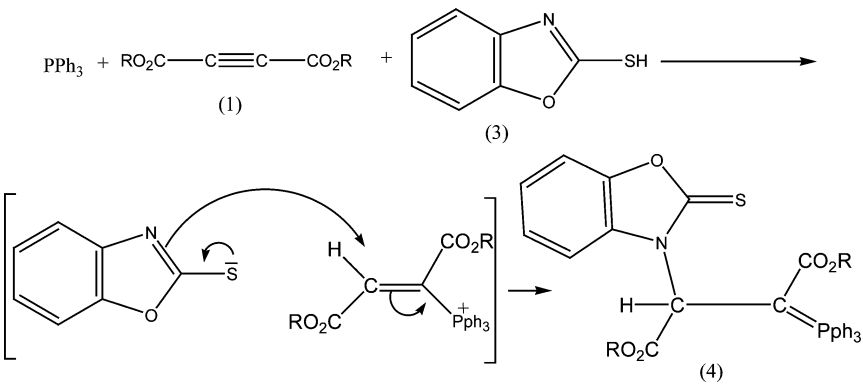
TABLE II Selected ^{1}H, ^{13}C, and ^{31}P NMR Chemical Shifts (δ in ppm) and Coupling Constants (J in Hz) for H-2, OR, CO_2R, C-2, C-3, and C=S in the Major (M) and Minor (m) Diastereoisomers of Compounds 4a–b

Compound	Isomer (%)	^{13}C NMR Data			^{1}H NMR Data			^{31}PNMR
		C-3(^{1}Jpc)	C-2(^{2}Jpc)	C=S	CO_2R	OR	H-2($^{3}J_{PH}$)	
4a	M(70)	40.60 (124.3)	62.78 (17.4)	180.09	3.22	3.78	5.81 (17.3)	24.11
4a	m(30)	41.38 (132.6)	62.83 (17.6)	180.33	3.71	3.79	5.62 (19.2)	25.08
4b	M	39.60 (124.0)	63.40 (17.7)	180.22	1.01	1.57	5.59 (18.6)	23.66

ylide **4** resulted from the initial addition of triphenylphosphine to the acetylenic ester and subsequent protonation of the 1:1 adduct by the SH-acid to form phosphoranes **4** (see Scheme 6).

The methoxy region of the ^{1}H NMR spectrum of **4a** in $CDCl_3$ at an ambient temperature (25°C) exhibited two sharp singlets for the CO_2CH_3 groups of (E) and (Z) isomers and two fairly broad singlets for the OCH_3 groups.

In summary, we have prepared novel 2-benzoxazolinone and 2-mercaptobenzoxazole phosphorus ylides using a one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong NH-acids, such as 2-benzoxazolinone, and SH-acids, such as 2-mercaptobenzoxazole. The present method carries the advantage that not only is the reaction performed under neutral conditions, but the substances can be mixed without any activation or modification. 2-benzoxazolinone and 2-mercaptobenzoxazole phosphorus ylides **3a–c** and **4a–b** may be considered potentially useful synthetic intermediates. The procedure described here may be an acceptable



SCHEME 6

method for the preparation of phosphoranes with variable functionalities.

EXPERIMENTAL

Melting points were measured on an Electrothermal 9100 apparatus. IR spectra were measured on a Shimadzu IR-460 spectrometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured with a BRUKER DRX-500 AVANCE spectrometer at 500.1, 125.8, and 202.4 MHz, respectively. Mass spectra were recorded on Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70eV. Triphenylphosphine, dialkyl acetylenedicarboxylates, 2-benzoxazolinone, and 2-mercaptobenzoxazole were obtained from Fluka (Buchs, Switzerland) and were used without further purification.

The Preparation of Dimethyl 2-(2-Benzoxazolinone-3-yl)-3-(triphenylphosphanylidene)butanedioate (3a)

General Procedure

To a magnetically stirred solution of 2-benzoxazolinone (0.14 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) in ethyl acetat (6 mL) was added dropwise a mixture of dimethyl acetylenedicarboxylate (0.12 ml, 1 mmol) in ethyl acetate (2 mL) at $-5^{\circ}C$ over 10 min. The reaction mixture was then allowed to warm up to r.t. and stand for 24 h. The solvent was removed under reduced pressure the solid residue was washed with cold diethyl ether (2×5 mL), and the product was obtained as a white powder, m.p. 163–164°C, 0.52 g, yield 98%. IR (KBr) (ν_{max}, Cm^{-1}): 1740 (C=O heterocyclic), 1620 and 1720 (C=O). MS (m/z, %): 540 (M, 2), 405 (M-heterocyclic, 100), 262 (PPh_3, 70), 183 (PPh_3—Ph, 60), 135 (heterocyclic, 18), 77 (Ph, 18).

Major isomer (E)-**3a**, ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.19 and 3.80 (6H, 2s, $2OCH_3$), 5.12 (1H, d, $^{3}J_{HP} = 16.4$ Hz, P—C—CH), 7.08–7.76 (19H, m, $3C_6H_5$ and C_6H_4) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 40.11 (d, $^{1}J_{cp} = 124.7$ Hz, P = C), 49.41 and 52.60 (2s, 2OMe), 57.79 (d, $^{2}J_{pc} = 16.5$ Hz, P—C—CH), 109.17, 113.01, 121.78, 123.82 (4s, 4CH, C_6H_4), 125.99 (d,$^{1}J_{cp} = 91.9$ Hz, C_{ipso}), 129.01 (d,$^{3}J_{pc} = 12.2$ Hz, C_{meta}), 130.04 (s, C—^{13}C—N heterocyclic), 132.44 (d,$^{4}J_{cp} = 2.7$ Hz, C_{para}), 133.43 (d,$^{3}J_{pc} = 10.0$ Hz, C_{ortho}), 142.54 (s, C—^{13}C—O heterocyclic), 153.75 (s, C=O heterocyclic), 169.62 (d,$^{3}J_{pc} = 12.5$ Hz C=O ester), 170.80 (d,$^{2}J_{pc} = 14.0$ Hz, P—C=C) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.71 (s, Ph_3P^{+}—C) ppm.

Minor isomer (Z)-**3a**, ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 3.70 and 3.79 (6H, 2s, $2OCH_3$), 5.04 (1H, d, $^{3}J_{HP} = 18.5$ Hz, P—C—CH), 7.08–7.76

(19H, m, $3C_6H_5$ and C_6H_4) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 40.46 (d, $^1J_{cp} = 134.4$ Hz, P=C), 50.37 and 52.31 (2s, 2OMe), 57.93 (d, $^2J_{pc} = 17.9$ Hz, P–C–CH), 109.49, 112.07, 121.74, 123.46 (4s, 4CH, C_6H_4), 125.34 (d,$^1J_{cp} = 91.7$ Hz, C_{ipso}), 129.05 (d,$^3J_{pc} = 12.2$ Hz, C_{meta}), 130.37 (s, C–^{13}C–N heterocyclic), 132.10 (d,$^4J_{cp} = 2.7$ Hz, C_{para}), 133.52 (d,$^3J_{pc} = 11.0$ Hz, C_{ortho}), 142.74 (s, C–^{13}C–O heterocyclic), 153.91 (s, C=O heterocyclic), 170.18 (d,$^3J_{pc} = 17.3$ Hz, C=O_{ester}), 170.91 (d,$^2J_{pc} = 13.8$ Hz, P–C=C) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.43 (s, Ph_3P^+–C) ppm.

Diethyl 2-(2-Benzoxazolinone-3-yl)-3-(triphenylphosphanylidene)butanedioate (3b)

White powder, m.p. 158–159°C, 0.51 g, yield 90%. IR (KBr) (ν_{max}, Cm^{-1}): 1767(C=O heterocyclic) 1673 and 1741 (C=O). MS (m/z, %): 568 (M, 2), 494(M–CO_2Et, 18), 432 (M-heterocyclic, 50), 262 (PPh_3, 50), 183.1 (PPh_3–PPh, 45), 135 (heterocyclic, 17).

Major isomer (E)-**3b**, ^1H NMR (500.1 MHz, $CDCl_3$): δ 0.50 and 1.31 (6H, 2t, $^3J_{HH} = 6.6$ Hz, 2O–C–CH_3), 3.75 and 4.22 (4H, 2m, ABX_3 system, 2O–CH_2–C), 5.10 (1H, d, $^3J_{HP} = 16.96$ Hz, P–C–CH), 7.07–7.81 (19H, m, $3C_6H_5$ and C_6H_4) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 14.02$ and 14.22 (2s, 2O=C–CH_3), 39.88 (d, $^1J_{cp} = 124.31$ Hz, P=C), 57.86 (d, $^2J_{cp} = 16.61$ Hz, P–C–CH), 58.08 and 61.53 (2s, O–CH_2–C), 109.09, 113.11, 121.67, 123.76 (4s, 4CH, C_6H_4), 126.22 (d,$^1J_{cp} = 91.9$ Hz, C_{ipso}), 128.93 (d,$^3J_{pc} = 12.4$ Hz, C_{meta}), 130.13 (s, C–^{13}C–N heterocyclic), 132.37 (d,$^4J_{cp} = 2.1$ Hz, C_{para}), 133.52 (d,$^2J_{pc} = 9.7$ Hz, C_{ortho}), 142.57 (s, C–^{13}C–O heterocyclic), 153.86 (s, C=O heterocyclic), 169.19 (d,$^3J_{pc} = 12.4$ Hz, C=O_{ester}), 170.20 (d,$^2J_{pc} =$ 13.9 Hz P–C=C) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.72 (s, Ph_3P^+–C) ppm.

Minor isomer (Z)-**3b**, ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.24 and 1.35 (6H, 2t, $^3J_{HH} = 6.7$ Hz, 2O–C=CH_3), 3.78 and 4.26 (4H, 2m, ABX_3 system, 2O–CH_2–C), 4.99 (1H, d, $^3J_{HP} = 21.2$ Hz, P–C–CH), 7.07–7.81 (19H, m, $3C_6H_5$ and C_6H_4) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta =$ 14.58 and 14.84 (2s, 2O–C=CH_3), 40.23 (d, $^1J_{cp} = 132.9$ Hz , P=C), 58.00 (d,$^2J_{cp} = 19.9$ Hz, P–C–CH), 58.78 and 61.47 (2s, O–CH_2=C), 109.44, 112.22, 123.28, 123.76 (4s, 4CH, C_6H_4), 125.62 (d,$^1J_{cp} = 92.0$ Hz, C_{ipso}), 128.98 (d,$^3J_{pc} = 12.3$ Hz, C_{meta}), 130.94 (s, C–^{13}C–N heterocyclic), 132.37 (d,$^4J_{cp} = 2.1$ Hz, C_{para}), 133.52 (d,$^2J_{pc} = 9.6$ Hz, C_{ortho}), 142.78 (s, C–^{13}C–O heterocyclic), 154.031 (s, C=O heterocyclic), 169.20 (d,$^3J_{pc} =$ 13.1 Hz, C=O_{ester}), 170.05 (d,$^2J_{CP} = 13.5$ Hz, P–C=C) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.81 (s, Ph_3P^+–C) ppm.

Di(tert-buthyl) 2-(2-Benzoxazolinone-3-yl)-3-(triphenylphosphanylidene)butanedioate (3c)

White powder, m.p. 189–190°C, 0.58 g, yield 94%. IR (KBr)(υ_{max}, Cm^{-1}): 1760 (C=O heterocyclic), 1610 and 1710 (C=O). MS (m/s, %): 624 (M, 2), 262 (PPh_3, 35), 183 (PPh_3—Ph, 50), 135 (heterocyclic, 25).

Only one isomer (E)-**3c**, ^1H NMR (500.1 MHz, $CDCl_3$): δ 1.02 and 1.59 (18H, 2s, $2CMe_3$), 4.95(1H, d, $^3J_{HP} = 17.7$ Hz, P—C—CH), 7.05–7.95 (19H, m, $3C_6H_5$, C_6H_4) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 28.06$ and 28.4 (2s, 2O—C—Me_3), 39.32 (d, $^1J_{cp} = 124.5$ Hz, P=C), 58.34 (d, $^2J_{pc} = 16.6$ Hz, P—C—CH), 77.63 and 81.24 (2s, O—CMe_3), 110.45, 112.35, 126.28, 127.01 (4s, 4CH, C_6H_4), 128.53 (d,$^1J_{cp} = 91.9$ Hz, C_{ipso}), 128.77 (d,$^3J_{pc} = 12.0$ Hz, C_{meta}), 130.22 (s, C—^{13}C—N heterocyclic), 132.26 (d,$^4J_{cp} = 2.5$ Hz, C_{para}), 133.57 (d,$^2J_{pc} = 9.5$ Hz, C_{ortho}), 142.58(s, C—^{13}C—O heterocyclic), 153.92 (s, C=O heterocyclic), 168.72 (d,$^3J_{pc} = 12.0$ Hz, C=O_{ester}), 168.46(d,$^2J_{pc} = 13.9$ Hz, P—C=C) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 23.30 (s, Ph_3P^+—C) ppm.

Dimethyl 2-(2-Mercaptobenzoxazole-3-yl)-3-(triphenylphosphanylidene)butanedioate (4a)

White powder, m.p. 194–195°C, 0.55 g, yield 96%. IR (KBr)(υ_{max}, Cm^{-1}): 1431(C=S), 1633, 1729(C=O). MS (m/z, %): 573(M, 1), 427(M—$2CO_2Me$, 2), 423 (M-heterocyclic, 2), 262 (PPh_3, 80), 183(PPh_3-Ph, 100), 140 (Heterocyclic, 5).

Major isomer(E)-**4a**, ^1H NMR (500.1MHz, $CDCl_3$): δ 3.22 and 3.78 (6H, 2S, $2OCH_3$), 5.8(1H, d, $^3J_{HP} = 17.3$ Hz, P—C—CH), 7.26, 7.33, 7.69 and 7.89 (4H, hetrocyclic), 7.41–7.6 (15H, m, $3C_6H_5$) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): δ 40.60 (d, $^1J_{PC} = 124.3$ Hz, P=C), 52.34 and 52.92 (2s, $2OCH_3$), 62.78 (d, $^2J_{PC} = 17.4$ Hz, P—C—CH), 109.73, 110.68, 123.54, 124.59, 131.73 and 148.78 (6C, hetrocyclic), 124.97 (d,$^1J_{PC} = 95.7$ Hz, C_{ipso}), 128.6 (d,$^3J_{PC} = 12.2$ Hz, C_{meta}), 132.1 (d,$^4J_{PC} = 2.1$ Hz, C_{para}), 133.44(d, $^2J_{PC} = 8.6$ Hz, C_{ortho}), 170.06 (d,$^3J_{PC} = 13.0$ Hz, C=O_{ester}), 170.15 (d,$^2J_{PC} = 12.9$ Hz, P—C=C), 180.09 (s, C=S) ppm. ^{31}P NMR (202.4 MHz, $CDCl_3$): δ 24.11 (Ph_3P^+—C) ppm.

Minor isomer (Z)-**4a**, ^1H NMR (500.1MHz, $CDCl_3$): δ 3.71 and 3.79 (6H, 2S, $2OCH_3$), 5.65 (1H, d, $^3J_{HP} = 19.2$ Hz, P—C—CH), 7.26, 7.33, 7.69 and 7.89 (4H, hetrocyclic), 7.41–7.6 (15H, m, $3C_6H_5$) ppm. ^{13}C NMR (125.8 MHz ,$CDCl_3$): δ 41.38 (d, $^1J_{PC} = 132.6$ Hz, P=C), 52.20 and 52.47 (2s, $2OCH_3$), 62.83 (d,$^2J_{PC} = 17.6$ Hz, P—C—CH), 109.88, 110.68, 123.37, 124.43, 131.14 and 148.78 (6C, hetrocyclic), 125.71 (d,$^1J_{PC} = 91.8$ Hz, C_{ipso}), 128.6 (d,$^3J_{PC} = 12.2$ Hz, C_{meta}), 132.53 (d,$^4J_{PC} = 2.0$ Hz, C_{para}), 133.51 (d, $^2J_{PC} = 9.1$ Hz, C_{ortho}), 170.8 (d, $^3J_{PC} = 13.2$ Hz,

$C{=}O_{ester}$), 170.55 (d, $^{2}J_{PC} = 13.4$ Hz, P–C=C), 180.33 (s, C=S) ppm. ^{31}P NMR (202.4 MHz ,$CDCl_3$): δ 25.08 (Ph_3P^{+}–C) ppm.

Di(tert-buthyl) 2-(2-Mercaptobenzoxazole-3-yl)-3-(triphenylphosphanylidene)butanedioate (4b)

White powder, m.p. 203–204°C, 0.59 g, yield 95%. IR (KBr)(υ_{max}, Cm^{-1}): 1477(C=S), 1636, 1742(C=O). MS (m/z, %): 629 (M, 5), 489 (M-heterocyclic, 25), 427 (M–$2CO_2$t–Bu, 2), 262 (PPh_3, 100), 183 (PPh_3–Ph, 90), 140 (heterocyclic, 2), 108 (PPh, 30).

Only one isomer(E)-**4b**, ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 1.0 and 1.57 (18H, 2s, CMe_3), 5.59 (1H, d, $^{3}J_{HP} = 18.6$ Hz, P–C–CH), 7.24, 7.29, 7.68 and 8.07 (4H, hetrocyclic), 7.41–7.63 (15H, m, $3C_6H_5$,) ppm. ^{13}C NMR (125.8 MHz, $CDCl_3$): $\delta = 28.01$ and 28.2 (2S, $2CMe_3$), 39.6 (d, $^{1}J_{PC} = 124.0$ Hz, P=C), 63.4 (d, $^{2}J_{PC} = 17.7$ Hz, P–C–CH), 77.96 and 81.51 (2S, $2CMe_3$), 109.39, 110.86, 123.24, 124.51, 131.11 and 148.75 (6C, hetrocyclic), 126.4 (d,$^{1}J_{PC} = 91.7$ Hz, C_{ipso}), 128.88 (d, $^{3}J_{PC} = 12.2$ Hz, C_{meta}), 132.18 (d, $^{4}J_{PC} = 2.0$ Hz, C_{para}), 133.57 (d, $^{2}J_{PC} = 9.0$ Hz, C_{ortho}), 167.95 (d, $^{3}J_{PC} = 13.2$ Hz, $C{=}O_{ester}$), 168.99 (d, $^{2}J_{pc} = 12.0$ Hz, P–C=C), 180.22 (s, C=S) ppm. ^{31}PNMR (202.4 MHz, $CDCl_3$): δ 23.66 (Ph_3P^{+}–C) ppm.

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