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Reaction of Lawesson's reagent with ester hydrazones: synthesis of novel 3-thioxo-1,2,3-diazaphospholine derivatives

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Reaction of Lawesson's reagent with ester hydrazones: synthesis of novel 3-thioxo-1,2,3-diazaphospholine derivatives

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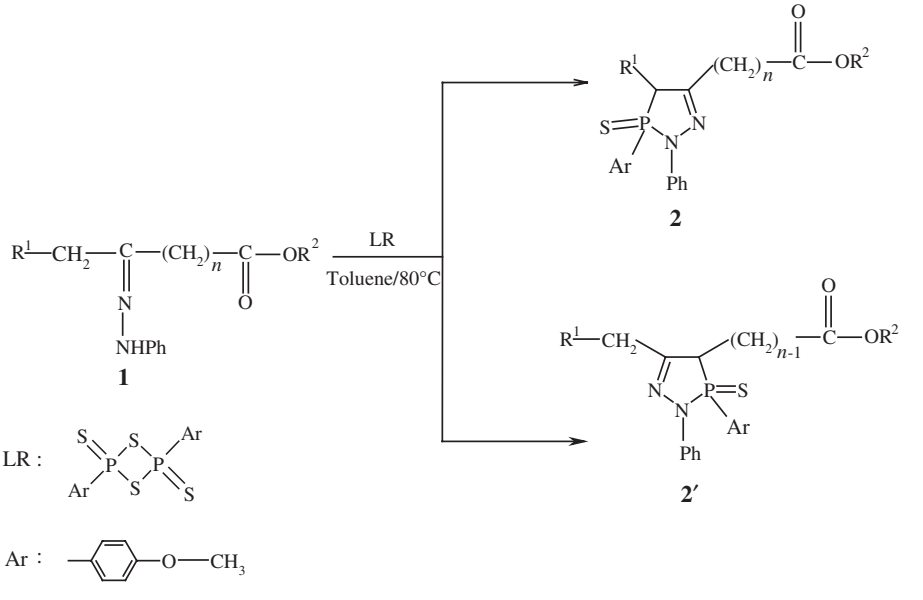
The reaction of ester hydrazones with Lawesson's reagent leads to a variety of new 3-thioxo-1,2,3-diazaphospholine derivatives. The reaction shows relative regioselectivity and gives in some cases a mixture of two diastereoisomers. The electronic and steric factors influencing the regioselectivity of the reaction are discussed.



1 **2** **2′**

Keywords: 3-thioxo-1,2,3-diazaphospholines; ester hydrazones; ketoesters; Lawesson's reagent; regioselectivity; diastereoisomers

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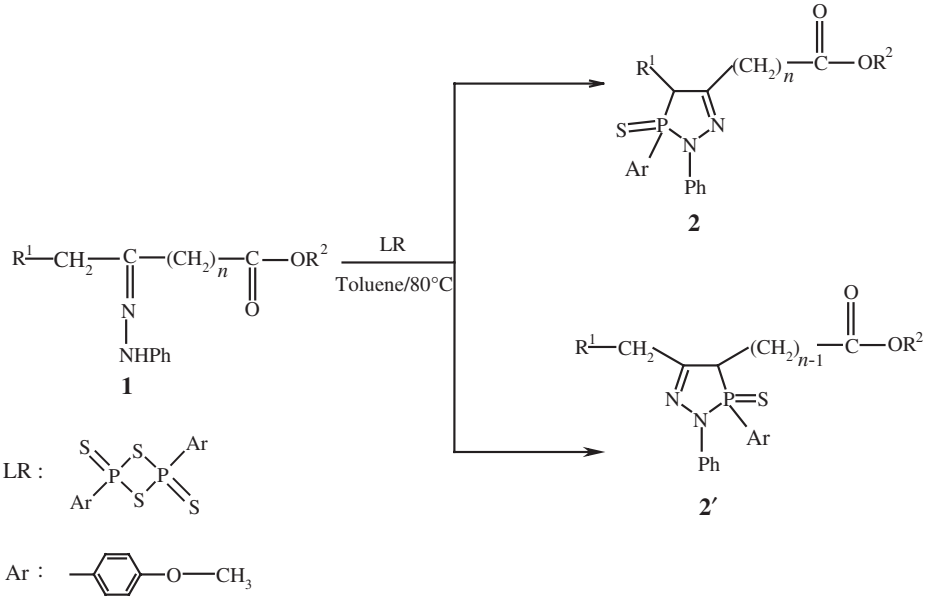
1. Introduction

The use of 2,4-bis(p-methoxyphenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide, commonly known as Lawesson's reagent (LR), for the synthesis of five- and six-membered phosphorus-containing heterocycles has been well documented (*1–4*). One of its important applications involves the synthesis of 3-thioxo-1,2,3-diazaphospholine derivatives by reaction with hydrazones (*5*). In this area, we have previously shown that β- and γ-phosphonylhydrazones react with LR to give 3-thioxo-1,2,3-diazaphospholine derivatives bearing an alkylphosphonate group (*6, 7*). We report, in the present investigation, the extension of this reaction to ester hydrazones **1**. Our main objective here was to study the effect of the ester group on the course of the reaction, in order to identify the factors which appear to govern regioselectivity in reactions of LR with hydrazones. The second goal of this work was the synthesis of a variety of new 3-thioxo-1,2,3-diazaphospholine derivatives, bearing an ester group.

It is important to note here that diazaphospholine derivatives are known for their useful properties ranging from antifungal (*8, 9*) to anticholinesterase (*10*) and antitumor (*11*) activities.

2. Results and discussion

The reaction of LR with an equimolar amount of ester hydrazone **1**, performed in toluene, at 80°C, leads according to the nature of substituents at the α, α' positions to the C = N double bond either



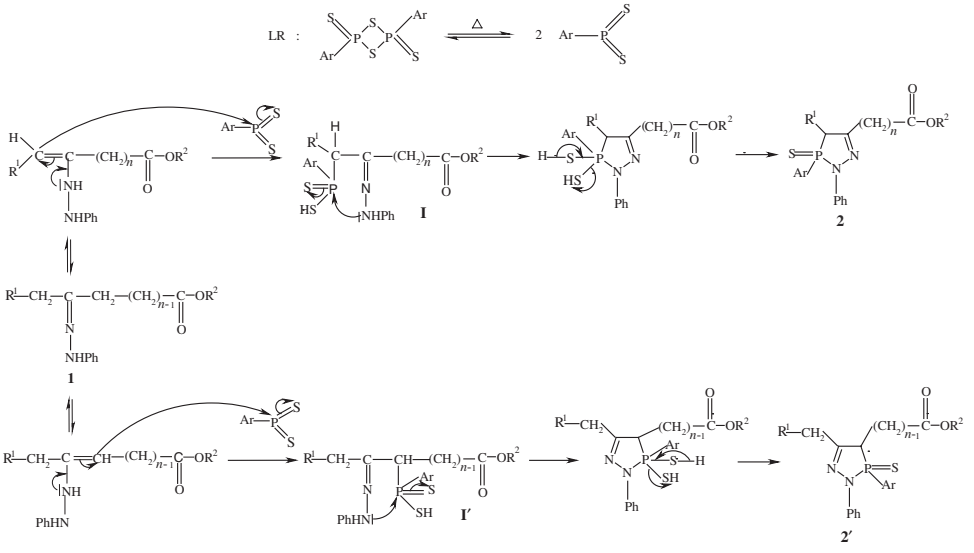
	2a	2b	2c	2d	2′a	2′b	2′c	2′e
R^1	H	Me	H	H	H	Me	H	(*)
R^2	Et	Me	Et	Et	Et	Me	Et	Et
n	1	1	2	0	1	1	2	1

Note: (*) $-CH_2-R^1$: Ph

Scheme 1. Synthesis of 3-thioxo-1,2,3-diazaphospholines **2** and **2′**.

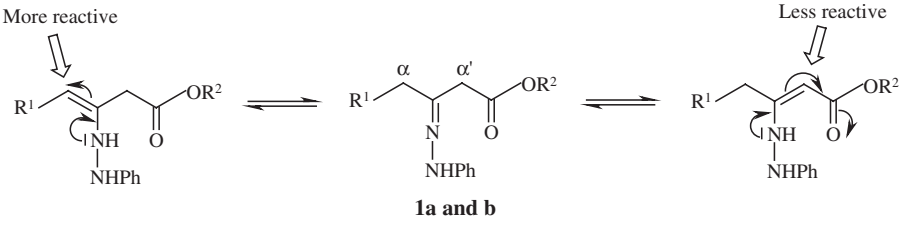
to the diazaphospholine derivative **2** or **2′** or to a mixture of isomeric diazaphospholines (**2** + **2′**) (Scheme 1). The reaction times (r.t.) range from 4 to 8 h depending on the nature of the substrate. The overall yield of the reaction is about 80%.

The reaction pathway was assumed to proceed via an equilibrium mixture of enehydrazines which react with LR leading to intermediates **I** and **I′**. These underwent intramolecular cyclization through the nucleophilic attack of the NH group at the phosphorus atom to give the final products **2** and **2′** (Scheme 2).



Scheme 2. Reaction mechanism for the synthesis of compounds **2** and **2′**.

We shall note here that the reaction shows relative regioselectivity. Indeed, when a mixture of **2** and **2′** regioisomers is possible, the reaction leads to an approximately 3:1 ratio of compounds **2**:**2′**. The regioselectivity of the reaction is governed by electronic and steric factors and depends essentially on the reactivity of carbons at the α and α' positions relative to the C = N double bond (Scheme 2). In the case of hydrazones **1a** and **b**, we can easily realize that the α'-carbon is less nucleophilic than the other one because of the conjugation with the ester group (Scheme 3). As for the hydrazone **1c**, and in the absence of conjugation with the ester function, the reaction becomes subject to steric control and takes place mainly at the less hindered α-carbon.



Scheme 3. Effect of the conjugation with the ester group on the reactivity of α and α' carbons.

Compounds **2** and **2′** were characterized on the basis of their IR, NMR (^{1}H, ^{31}P, ^{13}C) and mass spectral data, which indicate that they are obtained, in some cases, as a mixture of two

Table 1. δ ^{31}P in ppm and % of diastereoisomers for compounds **2** and **2′**.

Compound	**2a**	**2b$_1$**	**2b$_2$**	**2c**	**2d**	**2′a$_1$**	**2′a$_2$**
δ ^{31}P	75.7	92.4	79.3	93.2	75.6	69.9	77.1
% diastereoisomers	–	55	45	–	–	65	35
Compound	**2′b$_1$**	**2′b$_2$**	**2′c$_1$**	**2′c$_2$**	**2′e$_1$**	**2′e$_2$**	
δ ^{31}P	99.0	83.5	93.5	93.8	63.9	79.5	
% diastereoisomers	56	44	58	42	62	38	

diastereoisomers. This is due to the presence of a chiral carbon in addition to the asymmetric phosphorus atom. The major diastereoisomer will be designated by index 1 and the minor by index 2. The relative proportions of these diastereoisomers were estimated from the ^{31}P NMR spectra where a singlet for each diastereoisomer is present (Table 1).

The ^{13}C NMR spectra display the characteristic signals of all carbons and particularly those corresponding to the diazaphospholine ring. The C = N carbon resonates at 140–150 ppm. The C_4 carbon at the α position to the phosphorus atom gives a doublet toward 30 ppm. Such a doublet comes from the coupling with phosphorus with a $^1J_{CP}$ coupling constant of about 60–90 Hz.

3. Experimental section

^{1}H, ^{31}P and ^{13}C NMR spectra were recorded with $CDCl_3$ as the solvent, on a Bruker-300 spectrometer. The chemical shifts are reported in ppm relative to TMS (internal reference) for ^{1}H and ^{13}C NMR and relative to 85% H_3PO_4 (external reference) for ^{31}P NMR. The coupling constants are reported in Hz. For the ^{1}H NMR, the multiplicities of signals are indicated by the following abbreviations: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet.

Mass spectra were determined on an Agilent 5975B spectrometer, under electronic impact (EI) conditions. IR spectra were recorded on a Perkin Elmer Paragon 1000 PC spectrometer. The progress of the reactions was monitored by TLC. Purification of products was performed by column chromatography using silica gel 60 (Fluka).

3.1. *Synthesis of ester hydrazones 1*

To a mixture of phenylhydrazine (0.02 mol) in absolute ethanol (20 ml), cooled at 0°C, was added dropwise with stirring, a solution of ketoester (0.02 mol) in absolute ethanol (10 ml). Stirring at 0°C was continued for 12 h. The reaction mixture was then concentrated *in vacuo*. The solid obtained was washed with petroleum ether.

3.2. *Synthesis of 3-thioxo-1,2,3-diazaphospholines 2 and 2′*

A mixture of ester hydrazone **1** (0.01 mol), LR (0.01 mol) and dry toluene (30 ml) was heated at 80°C with stirring for the r.t. (the reaction was monitored by TLC). The reaction mixture was then concentrated *in vacuo*. The residue obtained was chromatographed on a silica gel column using ether as the eluent.

2a: Yellow oil; Yield = 64%; r.t. = 5 h; ^{1}H NMR ($CDCl_3$): δ = 1.15 (t, 3H, $^3J_{H-H}$ = 6.0 Hz, $C\underline{H}_3-CH_2$); 2.27 (s, 2H, $C\underline{H}_2-CO_2Et$), 3.71 (s, 3H, CH_3-O); 3.90 (q, 2H, $^3J_{H-H}$ = 6.0 Hz, $CH_3-C\underline{H}_2$); 3.93−4.11 (m, 2H, $CH_2-P(S)$); 6.10−7.67 (m, 9H, arom-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (J_{CP}): 13.5 ($\underline{C}H_3-CH_2-O$); 27.7 ($\underline{C}H_2-C=O$); 30.9 (87.2 Hz; $CH_2-P(S)$); 55.5 (CH_3-O); 65.8 ($CH_3-\underline{C}H_2-O$); 149.2 (C = N); 191.4 (C = O); Phenyl carbons: 113.2; 113.3; 113.5, 125.3; 127.9; 128.0; 128.5; 132.57; 132.63; 161.6; IR (neat): $\nu_{C=N}$ = 1585 cm^{-1};

$\nu_{P=S} = 1135\,cm^{-1}$; $\nu_{C=O} = 1784\,cm^{-1}$; EI-HRMS: calculated for $C_{19}H_{21}N_2O_3PS$, 388.1011 (M^+); found: 388.1018.

2b: Yellow oil; Yield = 53%; r.t. = 6 h; ^{1}H NMR ($CDCl_3$): δ = 1.26−1.46 (m, 3H, C<u>H</u>$_3$−CH); 2.08 (s, 2H, C<u>H</u>$_2$−CO_2Me, **2b**$_2$); 2.26 (s, 2H, C<u>H</u>$_2$−CO_2Me, **2b**$_1$); 3.37−3.53 (m, 1H, CH−P(S), **2b**$_1$), 3.59−3.70 (m, 1H, CH-P(S), **2b**$_2$); 3.68 (s, 3H, CH_3−O−C = O); 3.71 (s, 3H, CH_3−O); 6.07−7.77 (m, 9H, arom-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (J_{CP}): 11.9 (<u>C</u>H$_3$−CH, **2b**$_1$); 12.9 (<u>C</u>H$_3$−CH, **2b**$_2$); 20.5 (<u>C</u>H$_2$−C = O, **2b**$_1$); 21.3 (<u>C</u>H$_2$−C = O, **2b**$_2$); 28.8 (59.2 Hz; CH−P(S)); 51.6 (<u>C</u>H$_3$−O−CO, **2b**$_2$); 51.7 (<u>C</u>H$_3$−O−CO, **2b**$_1$); 55.4 (CH_3−O, **2b**$_1$); 55.5 (CH_3−O, **2b**$_2$); 154.4 (C = N, **2b**$_1$); 154.5 (C = N, **2b**$_2$); 195.8 (C = O, **2b**$_2$); 195.9 (C = O, **2b**$_1$); Phenyl carbons: δ = 102.1; 111.6; 112.67; 112.72; 112.8; 112.9; 116.1; 117.67; 117.70; 124.4; 124.5; 125.3; 126.0; 126.1; 126.4; 128.4; 131.8; 138.0; 160.1; 161.9; IR (neat): $\nu_{C=N} = 1562\,cm^{-1}$; $\nu_{P=S} = 1135\,cm^{-1}$; $\nu_{C=O} = 1760\,cm^{-1}$; EI-HRMS: calculated for $C_{19}H_{21}N_2O_3PS$, 388.1011 (M^+); found: 388.1034.

2c: Yellow oil; Yield = 58%; r.t. = 4 h; ^{1}H NMR ($CDCl_3$): δ = 1.02 (t, 3H, $^3J_{H-H}$ = 6.0 Hz, C<u>H</u>$_3$−CH_2); 2.11 (t, 2H, $^3J_{H-H}$ = 6.0 Hz, CH_2−C = N); 2.15 (t, 2H, $^3J_{H-H}$ = 6.0 Hz, CH_2−C = O); 2.72−2.85 (m, 2H, CH_2−P(S)); 3.55 (s, 3H, CH_3−O); 4.05 (q, 2H, $^3J_{H-H}$ = 6.0 Hz, CH_3−C<u>H</u>$_2$); 6.74−7.77 (m, 9H, arom-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (J_{CP}): 11.8 (<u>C</u>H$_3$−CH_2−O); 25.5 (<u>C</u>H$_2$−C = N); 28.3 (<u>C</u>H$_2$−C = O); 31.4 (55.1 Hz; CH_2−P(S)); 55.6 (CH_3−O); 60.4 (CH_3−<u>C</u>H$_2$−O); 144.7 (C = N); 194.9 (C = O); Phenyl carbons: 103.9; 110.8; 102.3; 120.9; 122.5; 125.4; 128.3; 133.1; 138.1; 162.9; IR (neat): $\nu_{C=N} = 1598\,cm^{-1}$; $\nu_{P=S} = 1127\,cm^{-1}$; $\nu_{C=O} = 1732\,cm^{-1}$; EI-HRMS: calculated for $C_{20}H_{23}N_2O_3PS$, 402.1167 (M^+); found: 402.1170.

2d: Yellow oil; Yield = 84%; r.t. = 4 h; ^{1}H NMR ($CDCl_3$): δ = 1.26 (t, 3H, $^3J_{H-H}$ = 9.0 Hz, C<u>H</u>$_3$−CH_2); 3.78 (s, 3H, CH_3−O); 3.75−3.83 (m, 2H, CH_2−P(S)); 4.07 (q, 2H, $^3J_{H-H}$ = 9.0 Hz, CH_3-C<u>H</u>$_2$); 6.77-8.28 (m, 9H, arom-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (J_{CP}): 14.3 (<u>C</u>H$_3$−CH_2−O); 30.3 (98.1 Hz; CH_2−P(S)); 55.3 (CH_3−O); 65.9 (CH_3−<u>C</u>H$_2$−O); 144.3 (C = N); 189.6 (C = O); Phenyl carbons: 113.4; 113.5; 113.7; 113.9; 113.0; 114.2; 129.0; 132.7; 134.6; 162.4; IR (neat): $\nu_{C=N} = 1573\,cm^{-1}$; $\nu_{P=S} = 1127\,cm^{-1}$; $\nu_{C=O} = 1772\,cm^{-1}$; EI-HRMS: calculated for $C_{18}H_{19}N_2O_3PS$, 374.0854 (M^+); found: 374.0859.

2′a: Yellow oil; Yield = 22%; r.t. = 5 h; ^{1}H NMR ($CDCl_3$): δ = 1.06 (t, 3H, $^3J_{H-H}$ = 6.0 Hz, C<u>H</u>$_3$−CH_2, **2′a**$_2$); 1.23 (t, 3H, $^3J_{H-H}$ = 6.0 Hz, C<u>H</u>$_3$−CH_2, **2′a**$_1$); 1.99 (s, 3H, CH_3−C = N, **2′a**$_2$); 2.17 (s, 3H, CH_3−C = N, **2′a**$_1$); 3.57 (s, 1H, CH−P(S), **2′**); 3.60 (s, 3H, CH_3−O, **2′a**$_1$); 3.63 (s, 3H, CH_3−O, **2′a**$_2$); 3.83 (q, 2H, $^3J_{H-H}$ = 6.0 Hz, CH_3−C<u>H</u>$_2$, **2′a**$_2$); 3.95 (q, 2H, $^3J_{H-H}$ = 6.0 Hz, CH_3−C<u>H</u>$_2$, **2′a**$_1$); 5.37 (s, 1H, CH−P(S), **2′a**$_1$); 6.60−7.60 (m, 9H, arom-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (J_{CP}): 14.6 (<u>C</u>H$_3$−CH_2−O, **2′a**$_1$); 14.7 (<u>C</u>H$_3$−CH_2−O, **2′a**$_2$); 29.9 (71.7 Hz; CH−P(S)); 34.2 (<u>C</u>H$_3$−C = N); 55.7 (CH_3−O); 61.3 (CH_3−<u>C</u>H$_2$−O, **2′a**$_2$); 61.4 (CH_3−C<u>H</u>$_2$−O, **2′a**$_1$); 148.9 (C = N, **2′a**$_2$); 154.5 (C = N, **2′a**$_1$); 187.0 (C = O, **2′a**$_2$); 187.4 (C = O, **2′a**$_1$); Phenyl carbons: 112.9; 113.1; 113.3; 113.4; 122.5; 122.8; 124.1; 125.5; 126.6; 127.0; 127.6; 128.2; 128.7; 129.2; 131.2; 131.9; 135.8; 137.2; 161.4; 161.9; IR (neat): $\nu_{C=N} = 1564\,cm^{-1}$; $\nu_{P=S} = 1157\,cm^{-1}$; $\nu_{C=O} = 1732\,cm^{-1}$; EI-HRMS: calculated for $C_{19}H_{21}N_2O_3PS$, 388.1011 (M^+); found: 388.1020.

2′b: Yellow oil; Yield = 20%; r.t. = 6 h; ^{1}H NMR ($CDCl_3$): δ = 1.17 (t, 3H, $^3J_{H-H}$ = 6.0 Hz, C<u>H</u>$_3$−CH_2, **2′b**$_1$); 1.20 (t, 3H, $^3J_{H-H}$ = 6.0 Hz, C<u>H</u>$_3$−CH_2, **2′b**$_2$); 2.59 (q, 2H, $^3J_{H-H}$ = 6.0 Hz, CH_3−C<u>H</u>$_2$, **2′b**$_1$); 2.61 (q, 2H, $^3J_{H-H}$ = 6.0 Hz, CH_3−C<u>H</u>$_2$, **2′b**$_2$); 3.67 (s, 3H, CH_3−O−C = O); 3.72 (s, 3H, CH_3−O); 5.75 (s, 1H, CH−P(S)), 6.07−7.77 (m, 9H, arom-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (J_{CP}): 13.6 (<u>C</u>H$_3$−CH_2, **2′b**$_2$); 13.7 (<u>C</u>H$_3$−CH_2, **2′b**$_1$); 17.4 (CH_3−<u>C</u>H$_2$, **2′b**$_1$); 20.5 (CH_3−<u>C</u>H$_2$, **2′b**$_2$); 32.2 (95.2 Hz; CH−P(S)); 51.3 (<u>C</u>H$_3$−O−CO, **2′b**$_2$); 51.4 (<u>C</u>H$_3$−O−CO, **2′b**$_1$); 55.2 (CH_3−O, **2′b**$_1$); 55.3 (CH_3−O, **2′b**$_2$); 154.2 (C = N, **2′b**$_1$); 154.3 (C = N, **2′**); 196.1 (C = O); Phenyl carbons: 105.4; 112.5; 113.0; 114.0; 119.6; 123.5; 123.6; 124.4; 124.7; 124.8; 124.9; 125.0; 127.8; 128.1; 128.3; 131.6; 132.4; 138.5; 162.0; 163.2; IR (neat):

$\nu_{C=N} = 1562\,cm^{-1}$; $\nu_{P=S} = 1135\,cm^{-1}$; $\nu_{C=O} = 1760\,cm^{-1}$; EI-HRMS: calculated for $C_{19}H_{21}N_2O_3PS$, 388.1011 (M^+); found: 388.1026.

2′c: Yellow oil; Yield = 31%; r.t. = 4 h; ^1H NMR ($CDCl_3$): δ = 1.09 (t, 3H, $^3J_{H-H} = 6.0$ Hz, C<u>H</u>$_3$−CH$_2$, **2′c**$_1$); 1.14 (t, 3H, $^3J_{H-H} = 6.0$ Hz, C<u>H</u>$_3$−CH$_2$, **2′c**$_2$); 1.67 (s, 3H, CH$_3$−C = N, **2′c**$_2$); 1.86 (s, 3H, CH$_3$−C = N, **2′c**$_1$); 2.68−2.82 (m, 2H, CH$_2$−C = O); 2.88 (t, 1H, $^3J_{H-H} = 9.0$ Hz, CH−P(S)); 3.55 (s, 3H, CH$_3$−O, **2′c**$_2$); 3.57 (s, 3H, CH$_3$−O, **2′c**$_1$); 3.90 (q, 2H, $^3J_{H-H} = 6.0$ Hz, CH$_3$−C<u>H</u>$_2$, **2′c**$_2$); 3.94 (q, 2H, $^3J_{H-H} = 6.0$ Hz, CH$_3$−C<u>H</u>$_2$, **2′c**$_1$); 6.74−7.77 (m, 9H, arom-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (J_{CP}): 16.2 (<u>C</u>H$_3$−CH$_2$−O, **2′c**$_1$); 16.3 (<u>C</u>H$_3$−CH$_2$−O, **2′c**$_2$); 20.9 (<u>C</u>H$_3$−C = N, **2′c**$_1$); 23.1 (54.3 Hz; CH−P(S), **2′c**$_1$); 24.6 (<u>C</u>H$_3$−C = N, **2′c**$_2$); 31.2 (50.6 Hz; CH−P(S), **2′c**$_2$); 36.9 (<u>C</u>H$_2$−C = O, **2′c**$_1$); 39.9 (<u>C</u>H$_2$−C = O, **2′c**$_2$); 55.6 (CH$_3$−O, **2′c**$_1$); 55.7 (CH$_3$−O, **2′c**$_2$); 60.5 (CH$_3$−<u>C</u>H$_2$−O, **2′c**$_1$); 66.3 (CH$_3$−<u>C</u>H$_2$−O, **2′c**$_2$); 159.5 (C = N, **2′c**$_1$); 159.6 (C = N, **2′c**$_2$); 192.4 (C = O, **2′c**$_2$); 192.8 (C = O, **2′c**$_1$); Phenyl carbons: 113.9; 114.0; 114.11; 114.15; 114.3; 115.6; 127.0; 128.0; 129.0; 129.1; 129.2; 129.3; 129.4; 132.5; 132.6; 132.7; 132.8; 132.9; 163.0; 163.1; IR (neat): $\nu_{C=N} = 1598\,cm^{-1}$; $\nu_{P=S} = 1127\,cm^{-1}$; $\nu_{C=O} = 1732\,cm^{-1}$; EI-HRMS: calculated for $C_{20}H_{23}N_2O_3PS$, 402.1167 (M^+); found: 402.1168.

2′e: Yellow oil; Yield = 41%; r.t. = 8 h; ^1H NMR ($CDCl_3$): δ = 1.10 (t, 3H, $^3J_{H-H} = 6.0$ Hz, C<u>H</u>$_3$−CH$_2$, **2′e**$_2$); 1.17 (t, 3H, $^3J_{H-H} = 6.0$ Hz, C<u>H</u>$_3$−CH$_2$, **2′e**$_1$); 3.65 (s, 1H, CH−P(S)); 3.68 (s, 3H, CH$_3$−O, **2′e**$_1$); 3,71 (s, 3H, CH$_3$−O, **2′e**$_2$); 3.95 (q, 2H, $^3J_{H-H} = 6.0$ Hz, CH$_3$−C<u>H</u>$_2$, **2′e**$_1$); 3.97 (q, 2H, $^3J_{H-H} = 6.0$ Hz, CH$_3$−C<u>H</u>$_2$, **2′e**$_2$); 6.66−7.75 (m, 14H, arom-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ (J_{CP}): 14.2 (<u>C</u>H$_3$−CH$_2$−O, **2′e**$_2$); 15.0 (<u>C</u>H$_3$−CH$_2$−O, **2′e**$_1$); 30.7 (142.0 Hz; CH−P(S)); 55.4 (CH$_3$−O, **2′e**$_1$); 55.6 (CH$_3$−O, **2′e**$_2$); 61.7 (CH$_3$−<u>C</u>H$_2$−O, **2′e**$_2$); 66.0 (CH$_3$−<u>C</u>H$_2$−O, **2′e**$_1$); 151.7 (C = N, **2′e**$_2$), 151.9 (C = N, **2′e**$_1$); 192.8 (C = O); Phenyl carbons: 108.7; 112.5; 113.4; 113.6; 113.8; 114.3; 125.3; 125.9; 126.0; 126.3; 126.4; 127.4; 128.8; 128.9; 129.0; 129.3; 131.0; 131.3; 131.8; 134.2; 134.6; 135.4; 135.9; 137.7; 138.48; 138.54; 162.3; 162.5; IR (neat): $\nu_{C=N} = 1581\,cm^{-1}$; $\nu_{P=S} = 1140\,cm^{-1}$; $\nu_{C=O} = 1728\,cm^{-1}$; EI-HRMS: calculated for $C_{24}H_{23}N_2O_3PS$, 450.1167 (M^+); found: 450.1164.

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