Synthesis and dynamic ^{1}H NMR study of stable phosphorus ylides derived from reaction between heterocyclic NH-acids and triphenylphosphine in the presence of acetylenic esters

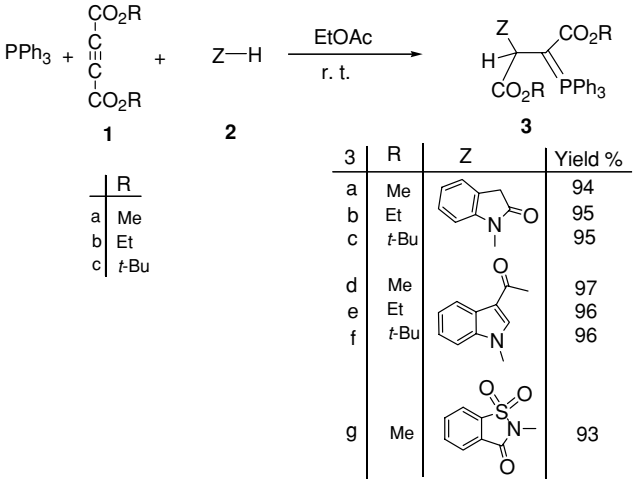
Nourollah Hazeri, Sayyed M. H. Khorassani, Malek T. Maghsoodlou*, Ghasem Marandi, Mahmoud Nassiri and Aqil G. Shahzadeh

Department of Chemistry, University of Sistan and Balouchestan, P. O. Box 98135-674, Zahedan, Iran

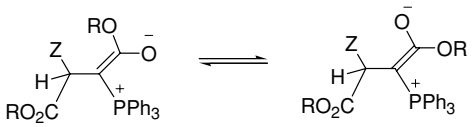
Stable crystalline phosphorus ylides are obtained in excellent yields from the 1:1:1 addition reaction between triphenylphosphine and dialkyl acetylenedicarboxylate in the presence of a strong NH-acid, such as 2-indolinone, 3-acetylindole and saccharine. These stable ylides exist in solution as a mixture of two geometrical isomers as a result of restricted rotation around the carbon–carbon partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group. Dynamic effects are observed in ^{1}H NMR spectra. The calculated free-energy of activation for interconversion of the rotational isomers in 2-indolinone amounts to about 68.2±2 J/mol.

Keywords: phosphorus ylides, NH-acids, acetylenic esters, dynamic NMR, restricted rotation

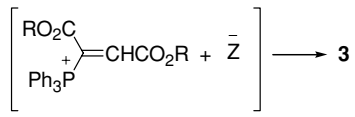
Phosphorus ylides are reactive systems, which take part in many valuable reactions in organic synthesis.[1-15] These ylides are most often prepared by treatment of a phosphonium salt with a base. The phosphonium salts are usually made from the phosphine and an alkyl halide[1-5] but they are also obtained by Michael addition of phosphus nucleophiles to activated olefins.[1,2] Here we describe an efficient synthetic route for the preparation of stable phosphorus ylides using triphenylphosphine, dialkyl acetylenedicarboxylates and strong NH-acids such as 2-indolinone, 3-acetylindole and saccharine. The reaction of triphenylphosphine with dialkyl acetylenedicarboxylate **1** in the presence of strong NH-acids **2** led to the corresponding stable heterocyclic phosphorus ylides **3** in excellent yield (see Scheme 1).



Scheme 1



Scheme 2



Scheme 3

Results and discussion

The reaction of 2-indolinone, 3-acetylindole and saccharine with dialkyl acetylenedicarboxylate **1** in the presence of triphenylphosphine was conducted in ethyl acetate solvent at room temperature and was complete within a few hours. The ^{1}H and ^{13}C NMR spectra of the crude product clearly indicated the formation of stable phosphorus ylides **3**. No other product could be detected by NMR spectroscopy. The structures of compounds **3a**–**g** were deduced from their IR, ^{1}H, ^{13}C, ^{31}P NMR and mass spectroscopic data. The mass spectra displayed molecular ion peaks at appropriate *m/z* values. Any initial fragmentations involve partial or complete loss of the side chains and scission of the heterocyclic ring system. The ^{1}H, ^{13}C and ^{31}P NMR spectrum of ylides **3a**, **3b**, **3d**, **3e**, **3g** are consistent with the presence of two isomers. The ylide moiety of these compounds is strongly conjugated with the adjacent carbonyl group and rotation around the partial double bond in (*E*)-**3** and (*Z*)-**3** geometrical isomers (see Scheme 2) is slow on the NMR timescale at ambient temperature.

Selected ^{1}H, ^{13}C and ^{31}P NMR chemical shifts and coupling constants in the major and minor geometrical isomers of compound **3** are shown in the experimental section. On the basis of the well established chemistry of trivalent phosphorus nucleophiles,[1-5] 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 to form phosphoranes **3** (see Scheme 3).

The methoxy region of the ^{1}H NMR spectrum of **3a** in $CDCl_3$ solvent at ambient temperature (25 °C) exhibits two sharp singlets for the CO_2CH_3 groups of the (*E*) and (*Z*) isomers and two fairly broad singlets for the OCH_3 groups. At near to 10 °C the broad lines become sharper.

The ^{1}H NMR of **3a** in 1,2-dichlorobenzene solvent at 10 °C is similar to that which was measured in $CDCl_3$ solvent (see Table 1). Increasing the temperature results in coalescence of the OCH_3 resonances.

Thus, at 90 °C, a relatively broad singlet was observed for the OCH_3 group, while the protons of CO_2CH_3 group appear as a sharp single resonance. Although, an extensive line-sharp analysis was not undertaken in relation to the dynamic ^{1}H NMR effect which would be observed for **3a,** nevertheless, the variable temperature spectrum allowed us to calculate[16]

* Correspondent. E-mail: MT_maghsoodlou@yahoo.com

Table 1 Selected proton chemical shift (at 500.1 MHz, in ppm, Me_4Si) and activation parameters (kJ mol^{-1}) for **3a** in 1,2-dichlorobenzene solvent

Compound	Temp/°C	Resonance (P–C–CO_2CH_3)	Δν/Hz	k/s	T_C/K	$\Delta G^{\neq}$
3a	15	3.67 3.75	40	89.7	328	68.23 ± 2
	90	3.72	–	–	–	–

the free energy of the barrier (if not the enthalpy and entropy of activation) for the dynamic NMR process in this ylide (see Table 1). The available experimental data are not suitable for obtaining meaningful values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$, even though the errors in $\Delta G^{\neq}$ are not large.[17]

In summary, we have prepared novel 2-indolinone, 3-acetylindole and saccharine-containing phosphorus ylides via one-pot reaction between triphenylphosphine and dialkyl acetylenedicarboxylates in the presence of strong NH-acids such as 2-indolinone, 3-acetylindole and saccharine. The present method, carries the advantage that, not only is the reaction performed under the neutral conditions, but also the substances can be mixed without any activation or modifications. It should be noticed that, 2-indolinone, 3-acetylindole and saccharine-containing phosphorus ylides **3a–g** may be considered as potentially useful synthetic intermediates. Dynamic NMR effects are observed in the ^{1}H NMR spectra of compound **3a** and are attributed to restricted rotation around the C–C partial double bond resulting from conjugation of the ylide moiety with the adjacent carbonyl group. It seems that the procedure described here may employed as be an acceptable method for the preparation of phosphoranes with variable functionalities.

Experimental

Melting points and IR spectra were obtained on an Electrothermal 9100 apparatus and a Shimadzu IR 470 spectrometer respectively. Elemental analyses for C, H and N were performed using a Heraeus CHN-O-Rapid analyser. The ^{1}H, ^{13}C and ^{31}P NMR spectrum were measured on a BRUKER DRX-500 AVANCE instrument with $CDCl_3$ as an solvent at 500.1, 125.8 and 202.4 MHz respectively. In addition, mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionisation potential of 70 ev. Dialkyl acetylendicarboxylates **1a**–**c**, 2-indolinone, 3-acetylindole and saccharine were obtained from Fluka (Buchs, Switzerland) and used without further purifications.

The preparation of dimethyl 2-(N-2-indolinone-1-yl)-3-(triphenylphosphanylidene)-butanedioate (**3a**): To a magnetically stirred solution of 2-indolinone (0.15 g or 1 mmol) and triphenylphosphine (0.26 g or 1 mmol) in 10 ml of ethyl acetate was added, dropwise, a mixture of dimethyl acetylenedicarboxylate (0.14 g or 1 mmol) in 4 ml of ethyl acetate at –5 °C over 10 min. After approximately 10 h stirring at room temperature, the product was filtered and recrystallised from ethyl acetate. White powder. m.p. 193–196 °C, yield: 0.51 g (94%), IR (KBr) (ν_{max}, cm^{-1}): 1743, 1702 and 1636 (C=O). Analyses: Calc. for $C_{32}H_{28}NO_5P$ (537.5): C, 71.5; H, 5.25; N, 2.6%; Found: C, 71.5; H, 5.1; N, 2.6%.

Major isomer (*E*)-**3a** (70 %), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 3.01 (1H, d, $^2J_{HH}$=22.1 Hz, CH_2), 3.12 (3H, s, OCH_3), 3.21 (1H, d, $^2J_{HH}$=22.1 Hz, CH_2), 3.77 (3H, s, OCH_3), 5.38 (1H, d, $^3J_{PH}$=16.4 Hz, P=C-CH), 7.01 (1H, t, *J*=7.4 Hz, CH_{arom}), 7.14 (1H, d, *J*=7.4 Hz, CH_{arom}), 7.32 (1H, t, *J*=7.7 Hz, CH_{arom}), 7.41–7.61 (15H, m, $3C_6H_5$), 7.72 (1H, d, *J*=7.4 Hz, CH_{arom}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 35.2 (CH_2), 38.7 (d, $^1J_{PC}$=123.4 Hz, P-C), 49.2 and 52.5 (2OCH3), 54.2 (d, $^2J_{PC}$=15.7 Hz, P–C–*CH*), 112.4–127.8 (6C, C_6H_4), 126.4 (d, $^1J_{PC}$=91.3 Hz, C_{ipso}), 128.8 (d, $^3J_{PC}$=12.3 Hz, C_{meta}), 132.1 (C_{para}), 133.5 (d, $^2J_{PC}$=9.7 Hz, C_{ortho}), 169.6 (d, $^3J_{PC}$=12.3 Hz, C=O), 171.5 (d, $^2J_{PC}$=15.2 Hz, P–C=*C*), 173.6 (NC=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 22.8 (Ph_3P^+–C).

Minor isomer (*Z*)-**3a** (30 %), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 3.06 and 3.26 (2H, 2d, $^2J_{HH}$=17.0 Hz, CH_2), 3.68 and 3.76 (6H, 2s, $2OCH_3$), 5.30 (1H, d, $^3J_{PH}$=18.5 Hz, CH), 6.99–7.02 (2H, m, $2CH_{arom}$), 7.13–7.17 (2H, m, $2CH_{arom}$), 7.42–7.60 (15H, m, $3C_6H_5$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 35.0 (CH_2), 39.4 (d, $^1J_{PC}$=132.6 Hz, P=C), 50.4 and 52.3 (2OCH3), 54.4 (d, $^2J_{PC}$=15.7 Hz, P=C–*CH*), 123.7–127.4 (6C, C_6H_4), 127.1 (d, $^1J_{PC}$=90.4 Hz, C_{ipso}), 128.8 (d, $^3J_{PC}$=12.3 Hz, C_{meta}), 132.1 (C_{para}), 133.6 (d, $^2J_{PC}$=9.9 Hz, C_{ortho}), 170.2 (d, $^3J_{PC}$=17.1 Hz, C=O), 171.6 (d, $^2J_{PC}$=18.5 Hz, P–C=*C*), 174.0 (NC=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.1 (Ph_3P^+–C).

Diethyl 2-(N-2-indolinone-1-yl)-3-(triphenylphosphanylidene) butanedioate (**3b**): White powder. m.p. 195–198 °C, yield: 0.54 g (95%), IR (KBr) (ν_{max}, cm^{-1}): 1741, 1707 and 1631 (C=O). Analyses: Calc. for $C_{34}H_{32}NO_5P$ (656.2): C, 62.2; H, 4.9; N, 2.1%; Found: C, 61.1; H, 4.85; N, 2.1%.

Major isomer (*E*)-**3b** (65 %), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.47 and 1.30 (6H, 2t, $^3J_{HH}$=7.1 Hz, $2OCH_2CH_3$), 3.03 and 3.28 (2H, 2d, $^2J_{HH}$=22.0 Hz,CH_2), 3.74 and 4.21 (4H, 2m, $2ABX_3$ system, $2OCH_2CH_3$), 5.35 (1H, d, $^3J_{PH}$=17.2 Hz, P=C-*CH*), 7.00 (1H, t, *J*=7.4 Hz, CH_{arom}), 7.14 (1H, d, *J*=6.9 Hz, CH_{arom}), 7.31 (1H, t, *J*=7.5 Hz, CH_{arom}), 7.42–7.62 (15H, m, $3C_6H_5$), 7.77 (1H, d, *J*=8.0 Hz, CH_{arom}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 14.0 and 14.2 ($2OCH_2CH_3$), 35.25 (CH_2), 38.4 (d, $^1J_{PC}$=122.7 Hz, P=C), 54.3 (d, $^2J_{PC}$=15.8 Hz, P=C–*CH*), 57.85 and 61.15 ($2OCH_2CH_3$), 112.6–127.7 (6C, C_6H_4), 126.6 (d, $^1J_{PC}$=91.3 Hz, C_{ipso}), 128.7 (d, $^3J_{PC}$=12.2 Hz, C_{meta}), 132.1 (d, $^4J_{PC}$=2.3 Hz, C_{para}), 133.6 (d, $^2J_{PC}$=9.7 Hz, C_{ortho}), 169.1 (d, $^3J_{PC}$=12.3 Hz, C=O), 170.9 (d, $^2J_{PC}$=14.7 Hz, P–C=*C*), 173.7 (NC=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 22.85 (Ph_3P^+–C).

Minor isomer (*Z*)-**3b** (35 %), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 1.24 and 1.34 (6H, 2t, $^3J_{HH}$=7.1 Hz, $2OCH_2CH_3$), 3.09 and 3.29 (2H, 2d, $^2J_{HH}$=22.3 Hz, CH_2), 4.09 and 4.29 (4H, 2m, $2ABX_3$ system, $2OCH_2CH_3$), 5.25 (1H, d, $^3J_{PH}$=19.3 Hz, P=C–*CH*), 6.98–7.00 (2H, m, $2CH_{arom}$), 7.17–7.25 (2H, m, $2CH_{arom}$), 7.41–7.65 (15H, m, $3C_6H_5$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 14.15 and 14.9 ($2OCH_2CH_3$), 35.05 (CH_2), 39.7 (d, $^1J_{PC}$=123.1 Hz, P=C), 54.45 (d, $^2J_{PC}$=15.9 Hz, P=C–*CH*), 58.7 and 61.1 ($2OCH_2CH_3$), 112.6–127.3 (6C, C_6H_4), 126.25 (d, $^1J_{PC}$=91.5 Hz, C_{ipso}), 128.75 (d, $^3J_{PC}$=12.1 Hz, C_{meta}), 132.05 (C_{para}), 133.6 (d, $^2J_{PC}$=9.7 Hz, C_{ortho}), 170.1 (d, $^3J_{PC}$=12.4 Hz, C=O), 170.7 (d, $^2J_{PC}$=18.8 Hz, P–C=*C*), 174.1 (NC=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.60 (Ph_3P^+–C).

Di-t-butyl 2-(N-2-indolinone-1-yl)-3-(triphenylphosphanylidene) butanedioate (**3c**): White powder. m.p. 197–200 °C, yield: 0.60 g (95%), IR (KBr) (ν_{max}, cm^{-1}): 1736, 1710 and 1638 (C=O). Analyses: Calc. for $C_{38}H_{40}NO_5P$ (621.26): C, 73.4; H, 6.4; N, 2.25%; Found: C, 73.3; H, 6.5; N, 2.1%.

Major isomer (*E*)-**3c**, ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 0.97 and 1.57 (18H, 2s, $2OCMe_3$), 3.10 (1H, 2d, $^2J_{HH}$=21.9 Hz, CH_2), 5.47 (1H, d, $^3J_{PH}$=18.2 Hz, P=C-*CH*), 6.98 (1H, t, *J*=7.4 Hz, CH_{arom}), 7.11 (1H, d, *J*=7.2 Hz, CH_{arom}), 7.31 (1H, t, *J*=7.7 Hz, CH_{arom}), 7.95 (1H, d, *J*=7.9 Hz, CH_{arom}) 7.37–7.67 (15H, m, $3C_6H_5$). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 28.2 and 28.4 ($2CMe_3$), 35.45 (CH_2), 37.7 (d, $^1J_{PC}$=122.5 Hz, P=C), 54.5 (d, $^2J_{PC}$=16.2 Hz, CH), 77.3 and 80.6 ($2OCMe_3$), 113.3–127.8 (6C, C_6H_4), 126.9 (d, $^1J_{PC}$=91.1 Hz, C_{ipso}), 128.5 (d, $^3J_{PC}$=12.2 Hz, C_{meta}), 131.9 (d, $^4J_{PC}$=1.9 Hz, C_{para}), 133.7 (d, $^2J_{PC}$=9.6 Hz, C_{ortho}), 168.7 (d, $^3J_{PC}$=11.8 Hz, C=O), 169.6 (d, $^2J_{PC}$=14.8 Hz, P–C=*C*), 173.7 (NC=O). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 22.5 (Ph_3P^+–C).

Dimethyl 2-(N-3-acetylindole-1-yl)-3-(triphenylphosphanylidene) butanedioate (**3d**)**:** White powder. m.p. 205–207 °C, yield: 0.53 g (97%), IR (KBr) (ν_{max}, cm^{-1}): 1746, 1637 and 1625 (C=O). MS (*m/z*, %): 564 (M^+, 2), 405 (M^+-heterocycle, 100), 262 (PPh_3, 55), 183 (M^+–2OMe–PPh_2, 58), 77 (Ph, 10). Analyses: Calc. for $C_{34}H_{30}NO_5P$ (563.2): C, 72.5; H, 5.3; N, 2.5%; Found: C, 72.6; H, 5.4; N, 2.5%.

Major isomer (*E*)-**3d** (53 %), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 2.54 (3H, s, CH_3), 3.27 and 3.71 (6H, 2s, $2OCH_3$), 4.92 (1H, d, $^3J_{PH}$=17.0 Hz, P=C-*CH*), 6.18 (1H, d, *J*=8.0 Hz, CH_{arom}), 6.92 (1H, t, *J*=7.0 Hz, CH_{arom}), 7.13 (1H, t, *J*=7.0 Hz, CH_{arom}), 7.30–7.60 (15H, m, $3C_6H_5$), 8.32 (1H, s, CH_{arom}), 8.43 (1H, s, CH_{arom}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 27.5 ($COCH_3$), 43.3 (d, $^1J_{PC}$=126.0 Hz, P=C), 49.6 and 52.8 (2OMe), 59.2 (d, $^2J_{PC}$=16.0 Hz, CH), 108.86–117.22–122.07–122.28–125.04–134.69–135.66 and 136.87 (8C, C_8H_5N), 126.1 (d, $^1J_{PC}$=92.0 Hz, C_{ipso}), 129.1 (d, $^3J_{PC}$=12.0 Hz, C_{meta}), 132.3 (C_{para}), 133.5 (d, $^2J_{PC}$=9.3 Hz, C_{ortho}), 170.0 (d, $^3J_{PC}$=12.3 Hz, C=O), 171.7 (d, $^2J_{PC}$=14.1 Hz, P–C=*C*), 193.5 ($COCH_3$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.9 (Ph_3P^+–C).

Minor isomer (*Z*)-**3d** (47 %), ^{1}H NMR (500.1 MHz, $CDCl_3$): δ_H 2.51 (3H, s, CH_3), 3.69 and 3.71 (6H, 2s, $2OCH_3$), 4.92 (1H, d, $^3J_{PH}$=17.0 Hz, P=C-*CH*), 6.24 (1H, d, *J*=8.0 Hz, CH_{arom}), 6.96 (1H, t,

J=7.0 Hz, CH_{arom}), 7.14 (1H, t, *J*=7.0 Hz, CH_{arom}), 7.28–7.60 (15H, m, $3C_6H_5$), 8.33 (1H, d, CH_{arom}), 8.43 (1H, s, CH_{arom}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 27.5 ($CO\mathit{C}H_3$), 43.6 (d, $^1J_{PC}$=135.1 Hz, P=C), 50.5 and 52.9 (2OMe), 58.7 (d, $^2J_{PC}$=15.8 Hz, P=C–*CH*), 108.98–117.22–122.19–122.68–126.20–134.67–135.66 and 136.99 (8C, C_8H_5N), 125.7 (d, $^1J_{PC}$=92.2 Hz, C_{ipso}), 129.1 (d, $^3J_{PC}$=12.0 Hz, C_{meta}), 132.3 (C_{para}), 133.5 (d, $^2J_{PC}$=9.1 Hz, C_{ortho}), 170.3 (d, $^3J_{PC}$=12.3 Hz, C=O), 171.6 (d, $^2J_{PC}$=14.1 Hz, P-C=*C*), 193.2 ($COCH_3$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 24.75 (Ph_3P^+–C).

Diethyl 2-(N-3-acetylindole-1-yl)-3-(triphenylphosphanylidene) butanedioate (**3e**): White powder. m.p. 157–159 °C, yield: 0.57 g (96%), IR (KBr) (ν_{max}, cm^{-1}): 1741, 1640 and 1632 (C=O). Analyses: Calc. for $C_{36}H_{34}NO_5P$ (591.2): C, 73.1; H, 5.75; N, 2.4%; Found: C, 73.1; H, 5.7; N, 2.4%.

Major isomer (*E*)-**3e** (70 %), ^1H NMR (500.1 MHz, $CDCl_3$): δ_H 0.54 and 1.21 (6H, 2t, *J*=7.0 Hz, $2OCH_2\mathit{CH}_3$), 2.54 (3H, s, CH_3), 3.83 and 4.25 (4H, 2m, $2ABX_3$, $2O\mathit{CH}_2CH_3$), 4.91 (1H, d, $^3J_{PH}$=16.0 Hz, P=C–*CH*), 6.19 (1H, d, *J*=8.0 Hz, CH_{arom}), 6.91 (1H, t, *J*=8.0 Hz, CH_{arom}), 7.09 (1H, t, *J*=8.0 Hz, CH_{arom}), 7.39–7.57 (15H, m, $3C_6H_5$), 8.31 (1H, d, *J*=8.0 Hz, CH_{arom}), 8.43 (1H, s, CH_{arom}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 14.1 and 14.3 ($2OCH_2\mathit{CH}_3$), 27.4 ($CO\mathit{C}H_3$), 43.3 (d, $^1J_{PC}$=126.57 Hz, P=C), 58.2 ($O\mathit{C}H_2CH_3$), 59.1 (d, $^2J_{PC}$=15.9 Hz, CH), 61.85 ($O\mathit{C}H_2CH_3$), 108.94–117.12–121.96–122.2i–126.08–135.13–136.03 and 136.98 (8C, C_8H_5N), 125.9 (d, $^1J_{PC}$=92.4 Hz, C_{ipso}), 129.05 (d, $^3J_{PC}$=11.0 Hz, C_{meta}), 132.4 (C_{para}), 133.5 (d, $^2J_{PC}$=10.9 Hz, C_{ortho}), 170.0 (d, $^3J_{PC}$=12.8 Hz, C=O), 171.8 (d, $^2J_{PC}$=13.7 Hz, P–C=*C*), 193.5 ($COCH_3$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.8 (Ph_3P^+–C).

Minor isomer (*Z*)-**3e** (30 %), ^1H NMR (500.1 MHz, $CDCl_3$): δ_H 1.21 and 1.26 (6H, 2t, *J*=7.0 Hz, $2OCH_2\mathit{CH}_3$), 2.52 (3H, s, CH_3), 4.13 and 4.26 (4H, 2m, $2ABX_3$, $2O\mathit{CH}_2CH_3$), 4.91 (1H, d, $^3J_{PH}$=16.0 Hz, P=C–*CH*), 6.23 (1H, d, *J*=8.0 Hz, CH_{arom}), 6.94 (1H, t, *J*=8.0 Hz, CH_{arom}), 7.12 (1H, t, *J*=8.0 Hz, CH_{arom}), 7.32–7.57 (15H, m, $3C_6H_5$), 8.31 (1H, d, *J*=8.0 Hz, CH_{arom}), 8.44 (1H, s, CH_{arom}). ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 14.0 and 14.3 ($2OCH_2\mathit{CH}_3$), 27.2 ($CO\mathit{C}H_3$), 43.7 (d, $^1J_{PC}$=134.9 Hz, P=C), 58.6 (d, $^2J_{PC}$=15.9 Hz, CH), 58.3 and 61.7 ($2O\mathit{C}H_2CH_3$), 108.73–117.10–121.96–122.08–125.03–135.13–136.07 and 137.04 (8C, C_8H_5N), 126.3 (d, $^1J_{PC}$=92.2 Hz, C_{ipso}), 129.05 (d, $^3J_{PC}$=11.1 Hz, C_{meta}), 132.3 (C_{para}), 133.6 (d, $^2J_{PC}$=11.0 Hz, C_{ortho}), 170.0 (d, $^3J_{PC}$=12.8 Hz, C=O), 170.8 (d, $^2J_{PC}$=13.7 Hz, P-C=*C*), 193.1 ($COCH_3$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 24.9 (Ph_3P^+–C).

Di-t-butyl 2-(N-3-acetylindole-1-yl)-3-(triphenylphosphanylidene) butanedioate (**3f**): White powder. m.p. 196–198 °C, yield: 0.61 g (96%), IR (KBr) (ν_{max}, cm^{-1}): 1727, 1632 and 1610 (C=O). Analyses: Calc. for $C_{40}H_{42}NO_5P$ (647.3): C, 74.2; H, 6.5; N, 2.2%; Found: C, 74.25; H, 6.45; N, 2.1%.

Major isomer (*E*)-**3f**, ^1H NMR (500.1 MHz, $CDCl_3$): δ_H 1.04 and 1.53 (18H, 2s, $2OCMe_3$), 2.55 (3H, s, CH_3), 4.72 (1H, d, $^3J_{PH}$=16.9 Hz, P=C–*CH*), 6.16 (1H, d, *J*=7.8 Hz, CH_{arom}), 6.88 (1H, t, *J*=7.8 Hz, CH_{arom}), 7.06 (1H, t, *J*=8.0 Hz, CH_{arom}), 7.36–7.57 (15H, m, $3C_6H_5$), 8.31 (1H, d, *J*=7.8 Hz, CH_{arom}), 8.55 (1H, s, CH_{arom}), ^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 28.3 and 28.4 ($2OC\mathit{Me}_3$), 27.2 ($CO\mathit{C}H_3$), 43.7 (d, $^1J_{PC}$=127.9 Hz, P=C), 59.5 (d, $^2J_{PC}$=16.2 Hz, P=C–*CH*), 77.9 and 81.3 ($2O\mathit{C}Me_3$), 108.89–116.93–121.76–122.17–126.05–133.62–136.34 and 137.09 (8C, C_8H_5N), 126.25 (d, $^1J_{PC}$=91.3 Hz, C_{ipso}), 128.8 (d, $^3J_{PC}$=12.1 Hz, C_{meta}), 132.3 (d, $^4J_{PC}$=1.7 Hz, C_{para}), 133.5 (d, $^2J_{PC}$=9.7 Hz, C_{ortho}), 169.2 (d, $^3J_{PC}$=12.2 Hz, C=O), 169.4 (d, $^2J_{PC}$=12.63 Hz, P–C=*C*), 193.4 ($COCH_3$). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.4 (Ph_3P^+–C).

Dimethyl 2-(1,1,3-trioxo-1,3-dihydrobenzo[d]isothiazol-2-yl)-3 (triphenylphosphanylidene)butanedioate (**3g**): White powder. m.p. 189.3–192.5 °C, yield: 0.55 g (93%), IR (KBr) (ν_{max}, cm^{-1}): 1737 and 1710 (C=O), 1362 (SO_2). Analyses: Calc. for $C_{31}H_{26}NO_7PS$ (587.6): C, 63.3; H, 4.4; N, 2.4%; Found: C, 63.3; H, 4.5; N, 2.4%. MS (*m/z*, %): 587 (M^+, 4), 277 (25), 262 (79), 183 (100), 147 (35), 108 (55), 76 (55).

Major isomer (*E*)-**3a** (56 %), ^1H NMR (500.1 MHz, $CDCl_3$): δ_H 3.78 and 3.80 (2OMe), 4.93 (1H, d, $^3J_{PH}$=20.1 Hz, P=C-*CH*), 7.33–7.82 (19H, m, $3C_6H_5$ and C_6H_4).^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 38.9 (d, $^1J_{PC}$=131.6 Hz, P=C), 49.0 and 52.5 (2OMe), 55.3 (d, $^2J_{PC}$=15.6 Hz, P–C–*CH*), 122.85–133.5 (6C, C_6H_4), 127.0 (d, $^1J_{PC}$=92.3 Hz, C_{ipso}), 128.8 (d, $^3J_{PC}$=12.9 Hz, C_{meta}), 133.6 (C_{para}), 133.6 (d, $^2J_{PC}$=9.2 Hz, C_{ortho}), 167.5 (NC=O), 169.1 (d, $^3J_{PC}$=13.8 Hz, C=O), 171.4 (d, $^2J_{PC}$=13.2 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 23.8 (Ph_3P^+–C).

Minor isomer (*Z*)-**3a** (44 %), ^1H NMR (500.1 MHz, $CDCl_3$): δ_H 3.18 and 3.63 (2OMe), 4.78 (1H, d, $^3J_{PH}$=20.0 Hz, P=C–*CH*), 7.31–7.82 (19H, m, $3C_6H_5$ and C_6H_4).^{13}C NMR (125.8 MHz, $CDCl_3$): δ_C 37.2 (d, $^1J_{PC}$=131.6 Hz, P=C), 49.0 and 50.4 (2OMe), 54.2 (d, $^2J_{PC}$=15.6 Hz, P–C–*CH*), 122.85–133.4 (6C, C_6H_4), 124.5 (d, $^1J_{PC}$=91.2 Hz, C_{ipso}), 128.5 (d, $^3J_{PC}$=13.1 Hz, C_{meta}), 133.1 (C_{para}), 133.7 (d, $^2J_{PC}$=8.9 Hz, C_{ortho}), 167.5 (NC=O), 169.1 (d, $^3J_{PC}$=13.8 Hz, C=O), 170.9 (d, $^2J_{PC}$=13.2 Hz, P–C=*C*). ^{31}P NMR (202.4 MHz, $CDCl_3$): δ_P 22.9 (Ph_3P^+–C).

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