Synthesis of functionalised phosphonates by three-component reaction between phosphites, dialkyl acetylenedicarboxylates and pyrrole, indole or benzotriazole

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Three-component reaction between dialkyl acetylenedicarboxylates, phosphites, and pyrrole, indole or benzotriazole leads to functionalised phosphonates in good yields.

Keywords: acetylenic esters, pyrrole, indole, benzotriazole, phosphonates, phosphites

The successful attack by nucleophilic trivalent phosphorus on a carbon atom is facilitated when the later is conjugated with a carbonyl group or when it is part of an unsaturated bond otherwise activated.[1-8] There have been many studies on reactions between trivalent phosphorus nucleophiles and unsaturated carbonyl compounds in the presence of a proton source such as an alcohol.[1] The reaction of phosphites and dimethyl acetylenedicarboxylate (DMAD) in the presence of naphthols reported to produce phosphonate derivatives.[9] Recently, the reaction between triphenylphosphite and dimethyl acetylenedicarboxylate in the presence of pyrrole or 2-ethylpyrrole was reported to produce pyrrole phosphonate esters.[10] In order to investigate the scope of this reaction and in continuation of our studies on the reaction between trivalent phosphorus nucleophiles and acetylenic esters in the presence of organic N–H[11] or O–H[9] acids, we decided to explore the reaction between different phosphites and dialkyl acetylenedicarboxylates in the presence of pyrrole, indole or benzotriazole.

Results and discussion

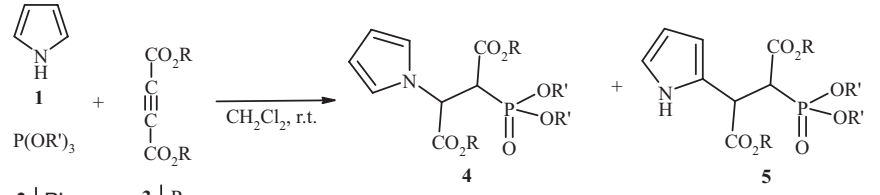
Pyrrole

We started our study on the reaction between triphenylphosphite, dimethyl acetylenedicarboxylate and pyrrole. Thus, after stirring an equimolar mixture of pyrrole **1,** DMAD **3a** and triphenylphosphite **2a** in dichloromethane for 12 hours we obtained phosphonate **5a** in 95% yield (Scheme 1).

The structures of all compounds were deduced from their elemental analyses and their IR, ^{1}H, ^{13}C, and ^{31}P NMR spectra. The mass spectra of these phosphonates are fairly similar and display molecular ion peaks.

The 500 MHz ^{1}H NMR spectrum of **5a** exhibits two signals, a double doublet at δ = 4.10 ppm and a triplet at δ = 4.74 ppm, for vicinal methine protons with $^2J_{HP}$ = 22 Hz, $^3J_{HP}$ = 11 Hz and $^3J_{HH}$ = 11 Hz. The vicinal proton–proton coupling constants can be obtained from the Karplus eqation.[12,13] Typically, J_{gauche} varies between 1.5 and 5 Hz and J_{anti} between 10 and 14 Hz. Observation of $^3J_{HH}$ = 11 Hz for vicinal protons in compound **5a** indicates an anti arrangement for these centres. Since compound **5a** possesses two stereogenic centres, two diastereomers with anti HCCH arrangements are possible (Scheme 2). The three-bond carbon–phosphorus coupling, $^3J_{CP}$, also depends on configuration, as expected, transoid couplings being larger than cisoid ones.[14] The observation of $^3J_{CP}$ = 2 Hz for the pyrrole carbon and $^3J_{CP}$ = 20 Hz for the ester C=O group, is in agreement with the (*2R,3S*)**-5a** and its mirror image geometries. The same isomer was previously reported as the only product of three-component reaction between triphenylphosphite, DMAD and pyrrole.[10] Some selected three-bond coupling constants for different isomers of compounds **5a**–**d** and **4d** are shown in Table 1.

Similar product **5b** with the same geometry was obtained from the three-component reaction between pyrrole, triphenylphosphite and diethyl acetylenedicarboxylate in 89% yield. However, when di-*tert*-butyl acetylenedicarboxylate was reacted with pyrolle and triphenylphosphite a 64 : 34 mixture of diastereomers of compound **5c** was obtained. The ratio of isomers was obtained from ^{1}H NMR spectra of compound **5c**. The three-bond hydrogen–hydrogen and carbon–phosphorus coupling constants for the major isomer is consistent with (2*RS*,3*SR*)**-5c,** as explained for compound **5a**. For minor isomer, the $^3J_{HH}$ coupling constant of 11 Hz for vicinal methine protons is consisted with the anti arrangement of these centres. The observation of $^3J_{CP}$ = 14 Hz for the pyrrole carbon and $^3J_{CP}$ = 6 Hz for the ester C=O group, is in agreement with the (*2S,3S*)**-5c** and its mirror image geometries.



2	R'
a	Ph
b	n-Bu
c	Me

3	R
a	Me
b	Et
c	t-Bu

4 , 5	R	R'	%Yield[b] of **4** (isomer ratio[a])	%Yield[b] of **5** (isomer ratio[a])
a	Me	Ph	-	95 (100:0)
b	Et	Ph	-	89(100:0)
c	t-Bt	Ph	-	90(64:36)
d	Me	n-Bu	34(61:39)	63(55:45)

[a](2 *RS*,3*SR*)/(2*SR*,3*SR*), obtained from ^{1}H NMR spectrum
[b]Isolated yield

Scheme 1

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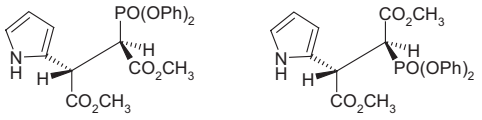


(*2R,3S*)-**5a** (*2S,3S*)-**5a**

Scheme 2

From the reaction between tributylphosphite, pyrrole and DMAD two products **4d** and **5d** were obtained, which were easily separated by column chromatography. In compound **4d**, pyrrole ring is substituted from nitrogen atom whereas in compound **5d** pyrrole ring bonded to the rest of the molecule from its carbon atom adjacent to nitrogen. Structures **4d** and **5d** are easily distinguished from their spectroscopic data. For example, the IR spectrum of compound **5d** shows an absorption bond at 3365 cm^{-1} for N–H stretching vibration. The NH proton of compound **5d** was exhibited at $\delta = 9.01$ ppm in ^1H NMR spectrum as a characteristic signal. In ^{13}C NMR spectrum of **5d** four signals are observed for pyrrole moiety, one of them is splitted to a doublet by phosphorus atom. ^{13}C NMR spectrum of **4d** shows two signals for pyrrole moiety which is inconsistent with the proposed structure. The NMR spectra of **4d** and **5d** show the presence of two diastereomers with nearly equal amounts. When we carried out the reaction between trimethylphosphite and DMAD or diethyl acetylenedicarboxylate in the presence of pyrrole the mixture of products**,** with pyrrole ring substituted from carbon or nitrogen atom**,** were obtained, which our efforts to separate them by chromatography were unsuccessful.

On the basis of the well-established chemistry of trivalent phosphorus nucleophiles[1-7] it is reasonable to assume that compounds **4** and **5** are resulted from the initial addition of phosphite to acetylenic ester and subsequent protonation of the 1 : 1 adduct by pyrrole (Scheme 3). Then, the positively charged ion **6** is attacked by the anion of pyrrole **7**. The attack of the conjugate anion of pyrolle may take place from nitrogen to produce ylid **8** or from carbon to form ylide **9**. These ylids are then hydrolysed to phosphonates **4** or **5** respectively.

Indole

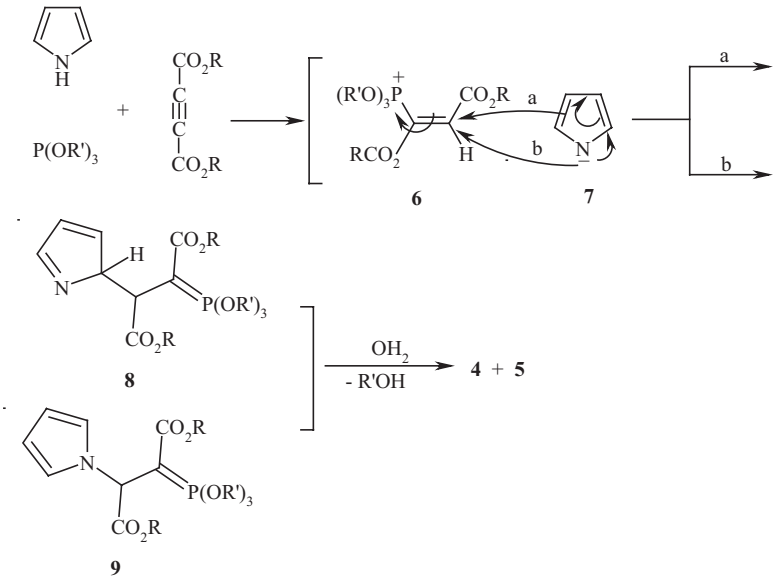
From the reaction between triphenylphosphite and DMAD in the presence of indole we obtained the phosphonate **11a,** in which the indole moiety is substituted at nitrogen atom, in 89% yield (Scheme 4). From the NMR data we realised that the product contained only (*2S,3S*)**-11a** diastereomer and its enantiomer (*2R,3R*)**-11a**. The three-component reaction of indole, trimethylphosphite and diethyl acetylenedicarboxylate was not diatereoselective, but only *N*-substituted product **11b** was isolated in 83% yield. However from the reaction between indole and DMAD in the presence of trimethylphosphite or tributylphosphite both of the *N*- and *C*-substituted indole derivatives were obtained as mixtures of diastereomers. As mentioned for compounds **4** and **5** compounds **11** and **12** were distinguished from their IR and NMR spectroscopic data. The IR and ^1H NMR spectra of compound **12c** showed the presence of a NH group in the structure of this compound. ^{13}C NMR spectrum of compound **12c** also confirmed the proposed structure; the signal related to C-3 of indole moiety is splitted by phosphorus atom to a doublet (see Experimental). Using three-bond H–H and C–P coupling constants, we are also able to recognise the stereochemistry of compounds **11** and **12**. Some characteristic coupling constants for different isomers are shown in Table 2.

Table 1 Selected three-bond coupling constants (Hz) for pyrrole phosphonate esters

Compound	Geometry	$3J_{HH}$	$3J_{CP}$ for C=O ester	$3J_{CP}$ for C2 pyrrole
5a	2*RS*,3*SR*	11	20	2
5b	2*RS*,3*SR*	11	20	2
5c	2*RS*,3*SR*	11	21	4
	2*RS*,3*SR*	8	8	14
5d	2*SR*,3*SR*	11	19	0
	2*SR*,3*SR*	9	7	19
4d	2*RS*,3*SR*	11	19	
	2*RS*,3*RS*	11	2	

Benzotriazole

The results of our study on the reaction between benzotriazole, acetylenic esters and phosphites are summarised in Scheme 5. From the reaction of benzotriazole and DMAD in the presence of triphenylphosphite no product was isolated. In fact, the only isolated compound was benzotriazole itself. However, benzotriazole reacted with DMAD or diethyl acetylenedicarboxylate in the presence of trimethylphosphite to yield the corresponding phosphonates as mixtures of diastereomers. The geometry of these compounds can be



Scheme 3

deduced from three-bond hydrogen–hydrogen and carbon–phosphorus coupling constants. Selected coupling constants are shown in Table 3.

In summary functionalised phosphonates may be prepared by a simple, one-pot reaction between acetylenic esters and phosphites in the presence of pyrrole, indole or benzotriazole. The present method carries the advantage that not only is the reaction performed under neutral conditions but also that the substances can be mixed without any activation or modification.

Experimental

All melting points are uncorrected. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyser. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionisation 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 Bruker DRX-500 Avance spectrometer at 500, 125.8, and 202.5 MHz, respectively. ^{1}H, ^{13}C and ^{31}P NMR spectra were obtained on solution in $CDCl_3$ using TMS as internal standard or 85% H_3PO_4 as external standard. Column chromatography was performed with Merck silica gel 60, 230–400 mesh. The chemicals used in this work purchased from Fluka (Buchs, Switzerland) and were used without further purification.

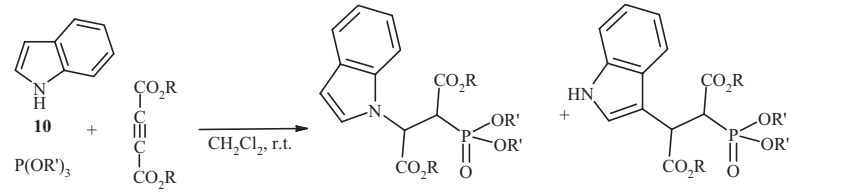
Dimethyl 2-(diphenoxyphosphoryl)-3-(pyrrol-2-yl) succinate (**5a**): Typical procedure: To a magnetically stirred solution of triphenylphosphite **2a** (0.31 g, 1 mmol) and pyrrole **1** (0.07 g, 1 mmol) in CH_2Cl_2 (10 ml) was added a mixture of dimethyl acetylenedicarboxylate **3a** (0.14 g, 1 mmol) in CH_2Cl_2 (5 ml) at room temperature. The reaction mixture was then stirred for 24 more hours at room 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 (4 : 1) mixture as eluent. White powder. m.p. 132–134°C, IR (KBr)(ν_{max}, cm^{-1}): 3290 (NH), 1726 (C=O, ester). Analyses: Calcd. for $C_{22}H_{22}NO_7P$: C, 59.6; H, 5.0; N, 3.2%. Found: C, 59.6; H, 4.9; N, 3.2%. MS (*m/z*,%): 443 (M, 15). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.7 and 3.8 (6 H, 2 s, 2 OCH_3), 4.1 (1 H. dd, $^{3}J_{HH}$ = 11 Hz, $^{2}J_{HP}$ = 22 Hz, CH), 4.7 (1 H, t, $^{3}J_{HH}$ = 11 Hz, $^{3}J_{HP}$ = 11 Hz, CH), 6.1–7.3 (13 H, aromatic protons), 8.8 (1 H, s, NH). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 43.21 (d, $^{2}J_{CP}$ = 1 Hz, CH), 49.22 (d, $^{1}J_{CP}$ = 136 Hz, CH), 52.86 and 53.08 (2 OCH_3), 108.30, 108.70, 118.61 (3 CH pyrrole), 120.23, 120.66 (2 d, $^{2}J_{CP}$ = 5Hz, 4 C_{ortho}), 123.88 (d, $^{3}J_{CP}$ = 2 Hz C pyrrole), 125.36 (d $^{5}J_{CP}$ = 2 Hz, 2 CH_{para}), 129.66, 129.70 (2 d, $^{4}J_{CP}$ = 1 Hz, 4 CH_{meta}) 149.65, 150.05

Table 2 Selected three-bond coupling constants (Hz) for indole phosphonate esters

Compound	Geometry	$3J_{HH}$	$3J_{CP}$ for C=O ester	$3J_{CP}$ for C2 pyrrole
11a	2*SR*,3*SR*	11	19	
11b	2*SR*,3*SR*	11	18	
	2*SR*,3*SR*	11	1	
11c	2*SR*,3*SR*	11	18	
	2*SR*,3*SR*	11	3	
11d	2*SR*,3*SR*	11	18	
	2*SR*,3*SR*	11	1	
12c	2*SR*,3*SR*	11	21	1
	2*SR*,3*SR*	11	1	18
12d	2*SR*,3*SR*	12	21	1
	2*SR*,3*SR*	11	1	17

Table 3 Selected three-bond coupling constants (Hz) for benzotriazole phosphonate esters

Compound	Geometry	$3J_{HH}$	$3J_{CP}$ for C=O ester	$3J_{CP}$ for C2 pyrrole
13b	2*SR*,3*SR*	11	18	
	2*SR*,3*SR*	11	2	
13c	2*SR*,3*SR*	11	18	
	2*SR*,3*SR*	11	2	



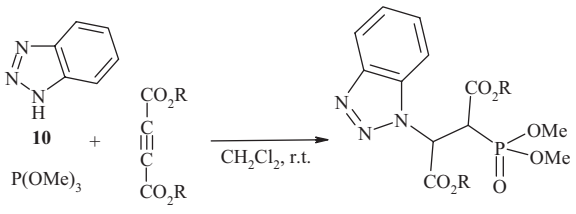
2	R'
a	Ph
b	n-Bu
c	Me

3	R
a	Me
b	Et

11 , 12	R	R'	%Yield[b] of **12** (isomer ratio[a])	%Yield[b] of **11** (isomer ratio[a])
a	Me	Ph	-	89 (100:0)
b	Et	Me	-	83(56:44)
c	Me	Me	39(57:43)	50(64:36)
d	Me	n-Bu	27(58:42)	75(55:45)

[a](2 *RS*,3*SR*)/(2*SR*,3*SR*), obtained from ^{1}H NMR spectrum
[b]Isolated yield

Scheme 4



3	R
a	Me
b	Et

13	R	%Yield[b] of **4** (isomer ratio[a])
a	Me	88(56:44)
b	Et	94(64:36)

[a](2*SR*,3*SR*)/(2*RS*,3*SR*), obtained from ^{1}H NMR spectrum
[b]Isolated yield

Scheme 5

(2 d, $^2J_{CP}$ = 10 Hz, 2 C_{ipso}), 167.96 (d, $^2J_{CP}$ = 5 Hz, C=O), 171.74 (d, $^3J_{CP}$ = 20 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.4 (P).

Diethyl 2-(diphenoxyphosphoryl)-3-(1H-pyrrol-2-yl) succinate (**5b**): Viscose oil. IR (KBr)(ν_{max}, cm^{-1}): 3375 (NH), 1735(C=O, ester). Analyses: Calcd. for $C_{24}H_{26}NO_7P$: C, 61.1; H, 5.6; N, 3.0%. Found: C, 61.4; H, 5.6; N, 3.1%. MS (*m/z*,%): 471 (M, 5). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23 (6 H, m, 2 CH_3), 4.1 (1 H.dd, $^3J_{HH}$ = 11Hz, $^2J_{HP}$ = 22Hz, CH), 4.2 (4 H, m, 2 OCH_2), 4.7 (1 H, t, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 11Hz, CH), 6.1–7.3 (13 H, aromatic protons), 8.9 (1 H, s, NH). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.94, 13.97 (2 CH3), 43.80 (d, $^2J_{CP}$ = 2 Hz, CH), 49.11 (d, $^1J_{CP}$ = 135 Hz, CH), 61.83, 62.22 (2 OCH_2), 108.32, 108.75, 118.43 (3 CH pyrrole), 120.27, 120.48 (2 d, $^2J_{CP}$ = 5Hz, 4 C_{ortho}), 124.15 (d, $^3J_{CP}$ = 2 Hz C pyrrole), 125.34, 125.40 (2 d $^5J_{CP}$ = 2 Hz, 2 CH_{para}), 129.66, 129.68 (2 d, $^4J_{CP}$ = 1 Hz, 4 CH_{meta}) 149.70, 150.17 (2 d, $^2J_{CP}$ = 10 Hz, 2 C_{ipso}), 167.26 (d, $^2J_{CP}$ = 5 Hz, C=O), 171.01 (d, $^3J_{CP}$ = 20 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.7 (P).

Di-tert-butyl2-(diphenoxyphosphoryl)-3-(1H-pyrrol-2-yl)succinate (**5c**): Viscose oil, IR (KB_r) (ν_{max}, cm^{-1}) (3278 (NH) 1731 (C=O, ester). Analyses: Calcd. for $C_{28}H_{34}NO_7P$: C, 63.7; H, 6.5; N, 2.7%. Found: C, 63.6; H, 6.4; N, 2.6%. MS (*m/z*,%): 527 (M, 5). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.1, 1.2 (18 H, 2 s, 6 CH_3), 3.9 (1 H, dd, $^3J_{HH}$ = 11Hz, $^2J_{HP}$ = 22Hz, CH), 4.6 (1 H, dd, $^3J_{HH}$ = 11 Hz, $^3J_{HP}$ = 11 Hz, CH), 6.1–7.3 (13 H, aromatic protons), 8.9 (1 H, s, NH). ^{13}C NMR (128.5.5 MHz, $CDCl_3$): δ 27.73, 27.77 (6 CH_3), 44.67 (d, $^2J_{CP}$ = 1 Hz, CH), 51.01 (d, $^1J_{CP}$ = 135 Hz, CH), 82.05, 82.88 (2 $OC(CH_3)_3$), 107.85, 108.58, 118.06 (3 CH pyrrole), 120.46, 120.71 (2 d, $^2J_{CP}$ = 5Hz, 4 C_{ortho}), 124.70 (d, $^3J_{CP}$ = 4 Hz C pyrrole), 125.23, 125.27 (d $^5J_{CP}$ = 2 Hz, 2 CH_{para}), 129.59, 129.66 (2 d, $^4J_{CP}$ = 1 Hz, 4 CH_{meta}) 149.84, 150.07 (2 d, $^2J_{CP}$ = 10 Hz, 2 C_{ipso}), 166.44 (d, $^2J_{CP}$ = 5 Hz, C=O), 170.53 (d, $^3J_{CP}$ = 21 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.0 (P). NMR data for (2S, 3R) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.3, 1.4 (18 H, 2 s, 6 CH_3), 4.1 (1 H, dd, $^3J_{HH}$ = 8Hz, $^2J_{HP}$ = 23Hz, CH), 4.6 (1 H, t, $^3J_{HH}$ = 8 Hz, $^3J_{HP}$ = 8 Hz, CH), 6.1–7.3 (13 H, aromatic protons), 9.0 (1 H, s, NH). ^{13}C NMR (128.5 MH_Z, $CDCl_3$): δ 27.77, 27.93 (6 CH_3), 44.24 (d, $^2J_{CP}$ = 2 Hz, CH), 48.76 (d, $^1J_{CP}$ = 132 Hz, CH), 82.16, 82.97 (2 $OC(CH_3)_3$), 108.00, 109.39, 118.15 (3 CH pyrrole), 120.46, 120.71 (2 d, $^2J_{CP}$ = 5H_Z, 4 C_{ortho}), 124.71 (d, $^3J_{CP}$ = 14 Hz C pyrrole), 125.27, 125.32 (d $^5J_{CP}$ = 2 Hz, 2 CH_{para}), 129.59, 129.70 (2 d, $^4J_{CP}$ = 1 Hz, 4 CH_{meta}) 150.18, 150.27 (2 d, $^2J_{CP}$ = 10 Hz, 2 C_{ipso}), 166.14 (d, $^2J_{CP}$ = 5 Hz, C=O), 169.81 (d, $^3J_{CP}$ = 8 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.3 (P).

Dimethyl 2-(dibutoxyphosphoryl)-3-(pyrrol-2-yl) succinate (**5d**): Viscose oil, IR (KB_r) (ν_{max}, cm^{-1}) (3365 (NH) 1735 (C=O, ester). Analyses: Calcd. for $C_{18}H_{30}NO_7P$: C, 53.6; H, 7.5; N, 3.5%. Found: C, 53.4; H, 7.3; N, 3.5%. MS (*m/z*,%): 403 (M, 5). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 0.80–1.71 (14 H, m, 2 CH_3 and 4 CH_2 of butyl groups), 3.72 and 3.78 (6 H, 2 s, 2 OCH_3), 3.84–4.15 (5 H, m, C*H*P and 2 OCH_2), 4.56 (1 H, t, $^3J_{HH}$ = 11H_Z, $^3J_{HP}$ = 11H_Z, CH), 6.11 (2 H, m, 2 CH of pyrrole), 6.72 (1 H, m, CH of pyrrole), 9.01 (1 H, s, NH). ^{13}C NMR (128.5 MH_Z, $CDCl_3$): δ 13.52 (2 CH_3), 18.53 and 18.61 (2 CH_2), 32.33 and 32.41 (2 CH_2), 43.05 (d, $^2J_{CP}$ = 2 Hz, *C*H), 48.43 (d, $^1J_{CP}$ = 132 Hz, *C*HP), 51.01 (2 OCH_3), 66.41 and 66.52 (2 d, $^2J_{CP}$ = 7 Hz, 2 $POCH_2$), 107.59, 109.12 and 118.08 (3 *C*H pyrrole), 124.39 (*C* pyrrole), 168.85 (d, $^2J_{CP}$ = 5 Hz, C=O), 172.20 (d, $^3J_{CP}$ = 19 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.6 (P). NMR data for (2*S*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 0.80–1.71 (14 H, m, 2 CH_3 and 4 CH_2 of butyl groups), 3.68 and 3.74 (6 H, 2 s, 2 OCH_3), 3.84–4.15 (5 H, m, C*H*P and 2 OCH_2), 4.37 (1 H, t, $^3J_{HH}$ = 9H_Z, $^3J_{HP}$ = 9H_Z, C*H*), 6.11 (2 H, m, 2 CH of pyrrole), 6.72 (1 H, m, CH of pyrrole), 9.01 (1 H, s, NH). ^{13}C NMR (128.5 MH_Z, $CDCl_3$): δ 13.56 (2 CH_3), 18.65 and 18.70 (2 CH_2), 32.18 and 32.27 (2 CH_2), 43.55 (*C*H), 49.67 (d, $^1J_{CP}$ = 129 Hz, *C*HP), 52.65 and 52.71 (2 OCH_3), 66.51 and 67.39 (2 d, $^2J_{CP}$ = 7 Hz, 2 $POCH_2$), 108.67, 109.37 and 118.47 (3 *C*H pyrrole), 124.57 (d, $^3J_{CP}$ = 13 Hz, C pyrrole), 168.43 (d, $^2J_{CP}$ = 5 Hz, C=O), 171.58 (d, $^3J_{CP}$ = 7 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.1 (P).

Dimethyl 2-(dibutoxyphosphoryl)-3-(pyrrol-1-yl) succinate (**4d**): Viscose oil, IR (KB_r) (ν_{max}, cm^{-1}) (1731 (C=O, ester). Analyses: Calcd. for $C_{18}H_{30}NO_7P$: C, 53.6; H, 7.5; N, 3.5%. Found: C, 53.6; H, 7.4; N, 3.6%. MS (*m/z*,%): 403 (M, 11). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 0.85–1.69 (14 H, m, 2 CH_3 and 4 CH_2 of butyl groups), 3.66 and 3.77 (6 H, 2 s, 2 OCH_3), 3.82–4.14 (5 H, m, C*H*P and 2 OCH_2), 5.17 (1 H, dd, $^3J_{HH}$ = 11H_Z, $^3J_{HP}$ = 9H_Z, CH), 6.11 (2 H, m, 2 C*H* of pyrrole), 6.72 (2 H, m, 2 C*H* of pyrrole). ^{13}C NMR (128.5 MH_Z, $CDCl_3$): δ 13.55 (2 CH_3), 18.54 and 18.64 (2 CH_2), 32.31 and 32.39 (2 CH_2), 48.27 (d, $^1J_{CP}$ = 132 Hz, *C*HP), 52.72 and 52.92 (2 OCH_3), 59.94 (d, $^2J_{CP}$ = 3 Hz, *C*H), 66.57 and 66.74 (2 d, $^2J_{CP}$ = 7 Hz, 2 $POCH_2$), 109.11, 120.57 (4 *C*H pyrrole), 167.55 (d, $^2J_{CP}$ = 6 Hz, C=O), 169.47 (d, $^3J_{CP}$ = 19 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.5 (P). NMR data for (2*S*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MH_Z, $CDCl_3$): δ 0.85–1.69 (14 H, m, 2 CH_3 and 4 CH_2 of butyl groups), 3.54 and 3.73 (6 H, 2 s, 2 OCH_3), 3.82–4.14 (5 H, m, C*H*P and 2 OCH_2), 5.32 (1 H, dd, $^3J_{HH}$ = 11H_Z, $^3J_{HP}$ = 7Hz, CH), 6.11 (2 H, m, 2 C*H* of pyrrole), 6.72 (2 H, m, 2 C*H* of pyrrole). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.64 (2 CH_3), 18.64 and 18.68 (2 CH_2), 32.22 and 32.30 (2 CH_2), 49.96 (d, $^1J_{CP}$ = 127 Hz, *C*HP), 53.00 and 53.17 (2 OCH_3), 59.79 (*C*H), 67.02 and 66.21 (2 d, $^2J_{CP}$ = 7 Hz, 2 $POCH_2$), 109.37, 120.44 (4 *C*H pyrrole), 166.20 (d, $^2J_{CP}$ = 6 Hz, C=O), 168.57 (d, $^3J_{CP}$ = 2 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.1 (P).

Dimethyl 2-(diphenoxyphosphoryl)-3-(indol-1-yl) succinate (**11a**)**:** Viscose oil, IR (KBr)(ν_{max}, cm^{-1}): 1726, 1732 (C=O, ester). Analyses: Calcd. for $C_{26}H_{24}NO_7P$: C, 63.3; H, 4.9; N, 2.8%. Found: C, 63.3; H, 4.9; N, 2.9%. MS (*m/z*,%): 493 (M, 7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.7, 3.8 (6 H, 2 s, 2 OCH_3), 4.1 (1 H. dd, $^3J_{HH}$ = 11 Hz, $^2J_{HP}$ = 21 Hz, CH), 6.0 (1 H, dd, $^3J_{HH}$ = 11 Hz, $^3J_{HP}$ = 8 Hz, CH), 6.6–7.6 (16 H, aromatic protons). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 48.53 (d, $^1J_{CP}$ = 135 Hz, CH), 57.69 (d, $^2J_{CP}$ = 1 Hz, CH), 53.36, 53.39 (2 OCH_3), 103.79, 109.87, 120.27, 121.31, 122.53, 124.10 129.11, 135.97 (indole carbons), 119.99, 120.53 (2 d, $^2J_{CP}$ = 5 Hz, 4 C_{ortho}), 125.28, 125.39 (2 d $^5J_{CP}$ = 2 Hz 2 CH_{para}), 129.66, 129.70 (2 d, $^4J_{CP}$ = 1 Hz, 4 CH_{meta}) 149.33, 149.74 (2 d, $^2J_{CP}$ = 10 Hz, 2 C_{ipso}), 166.78 (d, $^2J_{CP}$ = 6 Hz, C=O), 169.07 (d, $^3J_{CP}$ = 19 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13 (P).

Diethyl 2-(dimethoxyphosphoryl)-3-(indol-1-yl) succinate (**11b**)**:** Viscose oil, IR (KBr)(ν_{max}, cm^{-1}): 1731 (C=O, ester). Analyses: Calcd. for $C_{24}H_{36}NO_7P$: C, 54.4; H, 6.1; N, 3.5%. Found: C, 54.7; H, 6.3; N, 3.5%. MS (*m/z*,%): 397 (M, 9). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.12 and 1.23 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_3), 3.16 and 3.35 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 $POCH_3$), 3.68–4.24 (5 H, m, C*H*P and 2 OCH_2), 5.65 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 8 Hz, CH), 6.46 (1 H, m, C*H* of indole), 7.01–7.60 (5 H, m, 5 C*H* of indole). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 14.00 and 13.87 (2 CH_3), 49.04 (d, $^1J_{CP}$ = 128 Hz, *C*HP), 53.77 and 53.34 (2 d, $^2J_{CP}$ = 7 Hz, 2 $POCH_3$), 57.92 (CH), 62.32 and 62.40 (2 OCH_2), 103.84, 109.91, 120.17, 121.08, 122.26, 128.38 (6 *C*H indole), 128.95 and 135.88 (2 *C* indole), 166.92 (d, $^2J_{CP}$ = 6 Hz, C=O), 168.55 (d, $^3J_{CP}$ = 18 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.0 (P). NMR data for (2*S*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.96 and 1.09 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_3), 3.31 and 3.76 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 $POCH_3$), 3.68–4.24 (5 H, m, C*H*P and 2 OCH_2), 5.49 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 9 Hz, CH), 6.46 (1 H, m, C*H* of indole), 7.01–7.60 (5 H, m, 5 C*H* of indole). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.42 and 13.91 (2 *C*H_3), 46.10 (d, $^1J_{CP}$ = 134 Hz, *C*HP), 53.79 and 54.02 (2 d, $^2J_{CP}$ = 7 Hz, 2 $POCH_3$), 57.43 (CH), 62.02 and 62.32 (2 OCH_2), 103.36, 109.91, 120.21, 120.89, 122.21, 128.80 (6 *C*H indole), 130.90 and 136.41 (2 *C* indole), 165.44 (d, $^2J_{CP}$ = 6 Hz, C=O), 168.03 (d, $^3J_{CP}$ = 1 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.3 (P).

Dimethyl 2-(dimethoxyphosphoryl)-3-(indol-1-yl) succinate (**11c**)**:** Viscose oil, IR (KBr)(ν_{max}, cm^{-1}): 1726, 1732 (C=O, ester). Analyses: Calcd. for $C_{16}H_{20}NO_7P$: C, 52.0; H, 5.5; N, 3.8%. Found: C, 52.1; H, 5.7; N, 3.9%. MS (*m/z*,%): 369 (M, 17). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.16 and 3.35 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 $POCH_3$), 3.33 and 3.51 (6 H, 2 s, 2 OCH_3), 4.15 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 9 Hz, C*H*P), 5.71 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 8 Hz, C*H*), 6.45 (1 H, m, C*H* of indole), 7.02–7.61 (5 H, m, 5 C*H* of indole). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 47.27 (d, $^1J_{CP}$ = 133 Hz, *C*HP), 53.23 and 53.27 (2 OCH_3), 53.30 and 53.41 (2 d, $^2J_{CP}$ = 7 Hz, 2 $POCH_3$), 57.46 (CH), 103.47, 109.70, 120.27, 121.18, 122.40, 128.79 (6 *C*H indole), 130.91 and 135.79 (2 *C* indole), 167.51 (d, $^2J_{CP}$ = 6 Hz, C=O), 169.23 (d, $^3J_{CP}$ = 18 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.3 (P). NMR data for (2S, 3R) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.66 and 3.70 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 $POCH_3$), 3.60 and 3.74 (6 H, 2 s, 2 OCH_3), 4.23 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 9 Hz, C*H*P), 5.63 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 9 Hz, C*H*), 6.45 (1 H, m, C*H* of indole), 7.02–7.61 (5 H, m, 5 C*H* of indole). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 47.33 (d, $^1J_{CP}$ = 128 Hz, *C*HP), 53.23 and 53.27 (2 OCH3), 53.34 and 53.45 (2 d, $^2J_{CP}$ = 7 Hz, 2 $POCH_3$), 57.40 (CH), 104.03, 109.70, 120.27, 121.18, 122.34, 128.93 (6 *C*H indole), 132.41 and 135.79 (2 *C* indole), 167.75 (d, $^2J_{CP}$ = 6 Hz, C=O), 168.55 (d, $^3J_{CP}$ = 3 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.9 (P).

Dimethyl 2-(dimethoxyphosphoryl)-3-(indol-3-yl) succinate (**12c**)**:** Viscose oil, IR (KBr)(ν_{max}, cm^{-1}): 1726, 1732 (C=O, ester). Analyses: Calcd. for $C_{16}H_{20}NO_7P$: C, 52.0; H, 5.5; N, 3.8%. Found: C, 52.3;

H, 5.4; N, 3.9%. MS (*m/z*,%): 369 (M, 10). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.13 and 3.31 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 POC*H*$_3$), 3.35 and 3.51 (6 H, 2 s, 2 OC*H*$_3$), 4.10 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 9 Hz, C*H*P), 4.78 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 9 Hz, C*H*), 7.03–7.94 (5 H, m, 5 C*H* of indole), 8.74 (1 H, s, N*H*). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 41.50 (1 H, d $^2J_{CP}$ = 3 Hz, *C*H), 47.58 (d, $^1J_{CP}$ = 133 Hz, *C*HP), 53.33 and 53.42 (2 OCH_3), 53.52 and 53.61 (2 d, $^2J_{CP}$ = 7 Hz, 2 POCH_3), 108.67 (d $^3J_{CP}$ = 1 Hz, *C* of indole), 111.65, 118.95, 119.89, 122.14, 124.69, 125.93 (6 *C*H indole), 136.30 (*C* indole), 167.62 (d, $^2J_{CP}$ = 5 Hz, C=O), 172.90 (d, $^3J_{CP}$ = 21 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.0 (P). NMR data for (2*S*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): 3.43 and 3.47 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 POC*H*$_3$), δ 3.43 and 3.51 (6 H, 2 s, 2 OC*H*$_3$), 4.15 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 9 Hz, C*H*P), 4.93 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 8 Hz, C*H*), 7.03–7.94 (5 H, m, 5 C*H* of indole), 8.89 (1 H, s, N*H*). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 41.68 (*C*H), 49.26 (d, $^1J_{CP}$ = 127 Hz, *C*HP), 53.33 and 53.42 (2 OCH_3), 53.57 and 53.63 (2 d, $^2J_{CP}$ = 7 Hz, 2 POCH_3), 110.26 (d $^3J_{CP}$ = 18 Hz, *C* of indole), 111.40, 119.23, 119.84, 122.21, 123.47, 126.04 (6 *C*H indole), 136.03 (*C* indole), 169.22 (d, $^2J_{CP}$ = 5 Hz, C=O), 172.40 (d, $^3J_{CP}$ = 1 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.6 (P).

Dimethyl 2-(dibutoxyphosphoryl)-3-(indol-1-yl) succinate (**11d):** Viscose oil, IR (KBr)(ν_{max}, cm^{-1}): 1726, 1732 (C=O, ester). Analyses: Calcd. for $C_{22}H_{32}NO_7P$: C, 58.3; H, 7.1; N, 3.1%. Found: C, 58.3; H, 7.2; N, 3.3%. MS (*m/z*,%): 453 (M, 7). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.71–1.65 (14 H, m, 2 CH_3 and 4 CH_2 of butyl groups), 3.55 and 3.99 (6 H, 2 s, 2 OCH_3), 3.82–4.14 (5 H, m, C*H*P and 2 OCH_2), 5.78 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 9 Hz, C*H*), 6.49 (1 H, m, CH indole), 7.06–7.92 (5 H, m, 5 C*H* of indole). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.50 (2 CH_3), 18.53 and 18.65 (2 *C*H$_2$), 31.91 and 32.18 (2 *C*H$_2$), 47.58 (d, $^1J_{CP}$ = 133 Hz, *C*HP), 52.97 and 53.10 (2 OCH_3), 58.31 (1 H, d $^2J_{CP}$ = 3 Hz, *C*H), 103.87, 109.69, 120.15, 121.07, 122.21, 128.33 (6 *C*H indole), 132.40 and 135.69 (2 *C* indole), 167.66 (d, $^2J_{CP}$ = 5 Hz, C=O), 169.24 (d, $^3J_{CP}$ = 18 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.2 (P). NMR data for (2*S*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.71–1.65 (14 H, m, 2 CH_3 and 4 CH_2 of butyl groups), 3.32 and 3.63 (6 H, 2 s, 2 OCH_3), 3.82–4.14 (5 H, m, C*H*P and 2 OCH_2), 5.63 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 8 Hz, C*H*), 6.49 (1 H, m, CH indole), 7.06–7.92 (5 H, m, 5 C*H* of indole). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.39 (2 CH_3), 18.65 and 18.69 (2 *C*H$_2$), 31.99 and 32.36 (2 *C*H$_2$), 47.10 (d, $^1J_{CP}$ = 130 Hz, *C*HP), 52.57 and 52.91 (2 OCH_3), 57.85 (*C*H), 66.60 and 66.73 (2 d, $^2J_{CP}$ = 7 Hz, 2 POCH_2), 103.15, 109.75, 120.19, 120.87, 122.21, 129.08 (6 *C*H indole), 132.43 and 136.32 (2 *C* indole), 165.94 (d, $^2J_{CP}$ = 5 Hz, C=O), 168.50 (d, $^3J_{CP}$ = 1 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.1 (P).

Dimethyl 2-(dibutoxyphosphoryl)-3-(indol-3-yl) succinate (**12d):** Viscose oil, IR (KBr)(ν_{max}, cm^{-1}): 1726, 1732 (C=O, ester). Analyses: Calcd. for $C_{22}H_{32}NO_7P$: C, 58.3; H, 7.1; N, 3.1%. Found: C, 58.2; H, 7.2; N, 2.9%. MS (*m/z*,%): 453 (M, 13). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.74–1.69 (14 H, m, 2 CH_3 and 4 CH_2 of butyl groups), 3.56 and 3.81 (6 H, 2 s, 2 OCH_3), 3.89–4.20 (5 H, m, C*H*P and 2 OCH_2), 4.77 (1 H, dd, $^3J_{HH}$ = 12Hz, $^3J_{HP}$ = 9 Hz, C*H*), 7.06–7.76 (5 H, m, 5 C*H* of indole), 9.41 (1 H, s, N*H*). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.44 and 13.46 (2 CH_3), 18.62 and 18.67 (2 *C*H$_2$), 32.42 (d $^3J_{CP}$ = 7 Hz, 2 *C*H$_2$), 41.47 (d $^2J_{CP}$ = 3 Hz, *C*H), 47.48 (d, $^1J_{CP}$ = 133 Hz, *C*HP), 52.49 and 52.75 (2 OCH_3), 66.25 and 66.44 (2 d, $^2J_{CP}$ = 7 Hz, 2 OCH_2), 108.45 (d $^3J_{CP}$ = 1 Hz, *C* of indole), 111.74, 118.95, 119.69, 121.94, 124.98, 125.95 (6 *C*H indole), 136.49 (*C* indole), 169.48 (d, $^2J_{CP}$ = 5 Hz, C=O), 173.32 (d, $^3J_{CP}$ = 21 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.2 (P). NMR data for (2*S*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.74–1.69 (14 H, m, 2 CH_3 and 4 CH_2 of butyl groups), 3.33 and 3.62 (6 H, 2 s, 2 OCH_3), 3.89–4.20 (5 H, m, C*H*P and 2 OCH_2), 4.64 (1 H, t, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 11 Hz, C*H*), 7.06–7.76 (5 H, m, 5 C*H* of indole), 9.25 (1 H, s, N*H*). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.59 and 13.62 (2 CH_3), 18.54 and 18.59 (2 *C*H$_2$), 31.87 and 32.08 (2 d $^3J_{CP}$ = 7 Hz, 2 *C*H$_2$), 42.42 (*C*H), 48.61 (d, $^1J_{CP}$ = 126 Hz, *C*HP), 52.24 and 52.35 (2 OCH_3), 66.66 and 66.86 (2 d, $^2J_{CP}$ = 7 Hz, 2 OCH_2), 109.99 (d $^3J_{CP}$ = 17 Hz, *C* of indole), 111.51, 119.15, 119.63, 121.98, 123.60, 126.08 (6 *C*H indole), 136.12 (*C* indole), 167.73 (d, $^2J_{CP}$ = 5 Hz, C=O), 172.45 (d, $^3J_{CP}$ = 1 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 12.8 (P).

Dimethyl 2-(dimethoxyphosphoryl)-3-(benzotriazol-1-yl) succinate (**13a):** Viscose oil, IR (KBr)(ν_{max}, cm^{-1}): 1726, 1732 (C=O, ester). Analyses: Calcd. for $C_{14}H_{18}N_3O_7P$: C, 45.3; H, 4.9; N, 11.3%. Found: C, 45.3; H, 4.6; N, 11.4%. MS (*m/z*,%): 371 (M, 11). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.33 and 3.48 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 POC*H*$_3$), 3.66 and 3.89 (6 H, 2 s, 2 OC*H*$_3$), 4.44 (1 H, dd, $^3J_{HH}$ = 11Hz, $^2J_{HP}$ = 20 Hz, CH), 6.16 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 7 Hz, CH), 7.38–8.09 (4 H, m, 4 C*H* aromatic). ^{13}C NMR (128.5 MHz, $CDCl_3$):δ 45.27 (d, $^1J_{CP}$ = 131 Hz, *C*HP), 53.26 and 53.76 (2 d, $^2J_{CP}$ = 7 Hz, 2 POCH_3), 53.47 and 53.67 (2 OCH_3), 58.13 (d, $^2J_{CP}$ = 4 Hz, CH), 109.65, 120.02, 124.40, 128.26, 133.37, 145.56 (aromatic), 167.05 (d, $^2J_{CP}$ = 6 Hz, C=O), 167.28 (d, $^3J_{CP}$ = 18 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.2 (P). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 and 4.02 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 POC*H*$_3$), 3.53 and 3.78 (6 H, 2 s, 2 OC*H*$_3$), 4.75 (1 H, dd, $^3J_{HH}$ = 11Hz, $^2J_{HP}$ = 21 Hz, CH), 6.33 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 7 Hz, C*H*), 7.38–8.09 (4 H, m, 4 C*H* aromatic). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 45.64 (d, $^1J_{CP}$ = 129 Hz, *C*HP), 53.90 and 54.25 (2 d, $^2J_{CP}$ = 7 Hz, 2 POCH_3), 53.13 and 53.55 (2 OCH_3), 58.84 (d, $^2J_{CP}$ = 2 Hz, CH), 109.77, 120.11, 124.53, 128.30, 133.31, 145.47 (aromatic), 165.96 (d, $^2J_{CP}$ = 6 Hz, C=O), 166.59 (d, $^3J_{CP}$ = 2 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.2 (P).

Diethyl 2-(dimethoxyphosphoryl)-3-(benzotriazol-1-yl) succinate (**13b):** Viscose oil, IR (KBr)(ν_{max}, cm^{-1}): 1726, 1732 (C=O, ester). Analyses: Calcd. for $C_{16}H_{22}N_3O_7P$: C, 48.1; H, 5.6; N, 10.5%. Found: C, 48.4; H, 5.4; N, 10.5%. MS (*m/z*,%): 399 (M, 7). NMR data for (2*R*,3*R*) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 and 1.20 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_3), 3.32 and 3.44 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 POCH_3), 4.13–4.30 (4 H, m, 2 OCH_2), 4.44 (1 H, dd, $^3J_{HH}$ = 11Hz, $^2J_{HP}$ = 20 Hz, CH), 6.16 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 7 Hz, CH), 7.33–8.08 (4 H, m, 4 C*H* aromatic). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.64 and 13.86 (2 CH_3), 45.33 (d, $^1J_{CP}$ = 131 Hz, *C*HP), 53.15 and 53.48 (2 d, $^2J_{CP}$ = 7 Hz, 2 POCH_3), 58.34 (d, $^2J_{CP}$ = 4 Hz, CH), 62.39 and 62.85 (2 OCH_2), 109.74, 119.87, 124.27, 128.08, 133.26, 145.56 (aromatic), 166.32 (d, $^2J_{CP}$ = 6 Hz, C=O), 166.56 (d, $^3J_{CP}$ = 18 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.0 (P). NMR data for (2S, 3R) isomer and its enantiomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.07 and 1.38 (6 H, 2 t, $^3J_{HH}$ = 7 Hz, 2 CH_3), 3.77 and 3.87 (6 H, 2 d, $^3J_{HP}$ = 7 Hz, 2 POCH_3), 4.13–4.30 (4 H, m, 2 OCH_2), 4.78 (1 H, dd, $^3J_{HH}$ = 11Hz, $^2J_{HP}$ = 22 Hz, CH), 5.97 (1 H, dd, $^3J_{HH}$ = 11Hz, $^3J_{HP}$ = 8 Hz, C*H*), 7.33–8.08 (4 H, m, 4 C*H* aromatic). ^{13}C NMR (128.5 MHz, $CDCl_3$): δ 13.46 and 13.75 (2 *C*H$_3$), 45.74 (d, $^1J_{CP}$ = 130 Hz, *C*HP), 54.07 and 54.20 (2 d, $^2J_{CP}$ = 7 Hz, 2 POCH_3), 59.02 (d, $^2J_{CP}$ = 2 Hz, *C*H), 61.99 and 62.76 (2 OCH_2), 109.88, 119.77, 124.40, 128.08, 132.96, 145.32 (aromatic), 165.26 (d, $^2J_{CP}$ = 6 Hz, C=O), 165.95 (d, $^3J_{CP}$ = 2 Hz, C=O). ^{31}P NMR (202.5 MHz, $CDCl_3$): δ 13.4 (P).

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Reference

1 D.E.C. Corbridge, Phosphorus an outline of the chemistry, Biochemistry, and Uses (Elsevier, Amsterdam, 1995) 5th edn.
2 R. Engel, *Synthesis of Carbon-phosphorus bonds*, CRC Press, Boca Raton, FL, 1988.
3 O.I. Kolodiazhnyi, *Russ. Chem. Rev*., 1997, **66**, 225.
4 H.J. Bestmann and R. Zimmermann, *Top. Curr. Chem*., 1983, **109**, 85.
5 B.E. Maryano and A.B. Reits, *Chem. Rev*., 1989, **89**, 863.
6 K.M. Pietrusiewiz and M. Zablocka, *Chem. Rev*., 1994, **94**, 1375.
7 J.C. Tebby, in *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, ed. J.C. Verkede and L.D. Quin, VCH, Weinheim, ch. 1, pp 1-60, 1987.
8 M.V. George, S.K. Khetan and R.K. Gupta, *Adv. Heterocycl. Chem.,* 1976, **19**, 354.
9 I. Yavari and M. Anary-Abbasinejad, *Org. Biomol. Chem*., 2003, **3**, 560.
10 M.T. Maghsoodlou, S.M.H. Khorassani, R. Heydari and F.R. Charati, *J. Chem. Res*., 2006, 364.
11 (a) M. Anary-abbasinejad and N. Ascarrian, *J. Chem. Res*., 2007, 831; (b) M. Anary-abbasinejad and S. Tahan, *Phosphorus, Sulfur Silicon*, 2007, 315.
12 M. Karplus, *J. Am. Chem. Soc*., 1963, **88**, 2870.
13 C.A.G. Haasnot, F.A.A.M. De Leeuww and C. Altona, *Tetrahedron*, 1980, **36**, 2783.
14 E. Breitmaier and W. Voelter, *Carbon-13 NMR Spectroscopy*, 3rd edn., VCH, New York, 1990, p. 250.