Synthesis of diisopropyl pyridylphosphonates* 2"(B) *and* 3"(B)** (Scheme 1) ***by general procedure.[26] To a solution of diisopropyl phosphite (6.0 mmol, 1.0 mL) in dried MeCN (8 mL) was added corresponding bromo-derivative of pyridine (5.0 mmol methyl 5-bromonicotinate[25] **2'** or 2.5 mmol 3,5-dibromopyridine **3'**), *N*,*N*-diisopropylethylamine (6.0 mmol, 1.05 mL), palladium acetate (0.05 mmol, 14 mg) and 1,1'-bis(diphenylphosphino)ferrocene (dppf, 0.055 mmol, 31 mg) at room temperature. The reaction mixture was heated at 85 °C while continuously stirred under argon atmosphere for 24 h. Then the solvent was evaporated under reduced pressure. The residue was extracted with ethyl acetate (5, 2 and 2 mL), insoluble *N*,*N*-diisopropylethylamine hydrobromide was filtered off, dried in air and weight (gravimetric measurement of reaction yield). The filtrate was evaporate under reduced pressure to obtain a residue. The residue was subjected to column chromatography on silica gel using chloroform-ethyl acetate or ethanol-ethyl acetate as an eluent to obtain pure esters as oils. The eluates were monitored by TLC (R_f data are given in the experimental part below) The structures of final products **2"(B)** and **3"(B)** were confirmed by ^{1}H, $^{31}P\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ and data are given in the experimental section below.

Methyl 5-(diisopropoxyphosphoryl)nicotinate 2"(B): 1.0394 g, 69%, R_f=0.09 (silica gel on PET foils with fluorescent indicator 254 nm, $CHCl_3$-ethyl acetate=5:1 v/v, UV lamp for visualization). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (d, $^{3}J_{HH}$=5.9Hz, 6H, $POCCH_3$), 1.40 (d, $^{3}J_{HH}$=5.9Hz, 6H, $POCCH_3$), 3.98 (s, 3H, $COOCH_3$), 4.69-4.82 (m, 4H, POCH), 8.71 (d, $^{2}J_{PH}$=13.7Hz, 1H, pyridine ring), 9.11 (bs, 1H, pyridine ring), 9.34 (bs, 1H, pyridine ring). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 12.29 (s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.90 (d, $^{3}J_{CP}$=16.2Hz, POC<u>C</u>), 24.03 (d, $^{3}J_{CP}$=16.2Hz, POC<u>C</u>), 52.72 (s, COO<u>C</u>), 71.86 (d, $^{2}J_{CP}$=5.8Hz, PO<u>C</u>C), 125.69 (d, J_{CP}=24.7Hz, pyridine ring), 126.87 (d, J_{CP}=178 Hz, pyridine ring), 140.38 (d, J_{CP}=9.0Hz, pyridine ring), 153.38 (s, pyridine ring), 155.41 (d, J_{CP}=12.3Hz, pyridine ring), 164.89 (s, <u>C</u>$OOCH_3$).

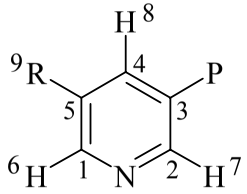
Tetraisopropyl 3,5-pyridinediyldiphosphonate 3"(B): 0.295 g, 29%, oil which solidified after standing, mp 57-58°C (hexane), R_f=0.06 (silica gel on PET foils with fluorescent indicator 254 nm, ethyl acetate, UV lamp for visualization). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (d, $^{3}J_{HH}$=6.2Hz, 12H, $POCCH_3$), 1.38 (d, $^{3}J_{HH}$=6.2Hz, 12H, $POCCH_3$), 4.75 (d x septet, $^{3}J_{HP}$=6.3Hz, 4H, POCH), 8.44 (t, $^{3}J_{HP}$=13.2 Hz, 1H, C4H), 9.08 (bs, 2H, C2H and C6H). $^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 12.77 (s). ^{13}C NMR (75 MHz, CDCl3): δ 23.96 (d, $^{3}J_{CP}$=12.9Hz, POC<u>C</u>), 71.86 (d, $^{2}J_{CP}$=2.6Hz, PO<u>C</u>C), 126.50 (d x d, $^{1}J_{CP}$=189Hz, $^{4}J_{CP}$=10.0Hz, C3 and C5), 142.41 (t, $^{2}J_{CP}$=8.8Hz, C4), 154.81 (d, $^{2}J_{CP}$=11.2Hz, C2 and C6).

Table S1 Observed vibrational bands and their assignment.

1	**2**	**3**	**Assignment**
3425 w, b	3420 w, b	3421 w, b	ν N−H
3250 w	3265 w	3260 m	ν C−H (ring)
3168 w	3200 w	3190 w-m	
3120 w		3138 w-m	
3087 m, n	3075 m-s	3106 sh	
3056 w	3025 w	3084 m	
		3040 m	
2650 m, b		~2660 m, vb	ν (P)O−H and/or ν (C)O−H
2550 window	~2400 m-s, b	2500 window	
2450 m	2273 window		
	2145 m-s		
2400 min	2185 m-s		
	2050 window	~2280 vb	
2250 b	2007 m-s	2000 window	
	1950 m-s		
1735 b	1885 vb		
		~ 1000 s, b	ν (P)O−H−O(P)
	1708 s		ν C=O
1630 vs	1624 m-s	1620 m-s	ν C=N (pyridyl ring) and ν C=C (pyridyl ring)
1582 s	1565 w-m	1605 s	
1552 s	1540 w	1550 m-s	
1463 s	1457 w		
	1430 sh		δ N−H
	1417 s, n	1405 s	
	1316 m, n		ν C−OH and/or δ O−H
	1266 vs, b		ν C−C
1370 s	1375 vw		ν P=O and/or ν PO_2
1355 m	1360 vw	1325 w	
1320 w, sh		1260 sh	
1275 m-s	1211 sh	1230 sh	
1192 vs	1176 vs	1205 s	
1148 s, sh			
1126 vs	1125 s	1133 vs	
1114 vs	1100 m	1070 vs	
1060 s, sh	1041 vs	1026 s	ν P−OH and ν P−C
1037 vs	1010 vs	1000 vs	
986 vs	978 m, sh	958 vs	
940 vs	955 vs	945 vs	
	937 vs		
921 sh	925 sh		
900 sh	915 vs		
	860 m	865 s, b	γ (C)O−H
807 vs	776 window	806 vs	ring deformation and
745 window	769 s, asym	758 sh	

730 s-vs, n	750 sh	701 window	ring torsion
685 vs, n	722 w	690	
	680 s, n	685	
	655 s, asym	676 vs	
628 s-vs, 550 vs 537 vs 520 vs 447 s	587 s	570 s	PO_3 deformations
	556 m, sh	552 vs	
	536 m		
	502 m		
	479 m	475 vs	
	440 m	441 s	
	415 m	413 s	

Table S2 Calculated and measured chemical shifts.

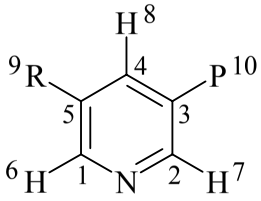


R = H, C or P

	1”			**2” (A)**					**3” (A)**				**1**	**2**	**3**
	Calculated		Exp.	Calculated				Exp.	Calculated			Exp.	Exp.	Exp.	Exp.
	⇑ [a]	⇓		↓⇑	↑⇑	↑⇓	↑⇓		⇓⇓	⇓⇑	⇑⇑				
1	156.88	157.09	152.89	157.16	157.72	158.07	157.88	152.31	161.3	159.89	158.83	155.05	148.31	148.93	142.43
2	156.20	155.02	152.11	159.98	159.87	161.15	159.29	154.05	161.29	160.64	158.29	155.05	142.06	151.71	142.43
3	129.74	130.90	124.94	132.01	131.19	130.10	132.35	124.25	129.78	130.00	131.35	125.32	136.57	136.26	134.99
4	144.50	142.00	139.45	143.84	144.95	143.19	142.99	139.84	146.55	147.74	145.61	142.73	142.18	139.00	148.37
5	127.10	127.08	123.38	133.25	134.83	133.57	134.91	123.28	129.78	130.44	131.64	125.32	127.33	132.45	134.99
6	8.41	8.40	8.69	9.02	8.82	9.08	8.83	9.34	8.71	8.60	8.55	9.10	8.62	8.70	8.73
7	8.50	8.50	8.89	8.65	8.65	8.76	8.66	9.10	8.71	8.68	8.54	9.10	8.71	8.63	8.73
8	7.73	7.56	8.02	7.91	8.36	7.74	8.21	9.71	7.77	7.85	7.84	8.39	8.58	8.23	8.66
9	7.04	6.99	7.32	-	-	-	-	163.04	-	-	-	-	7.91	162.41	-

[a] The arrow indicates the direction of the P=O (⇓ or ⇑) or C=O (↑ or ↓) vectors with respect to the N_{py} atom: toward (when pointing down) or out (when pointing up).

Table S3 Calculated and measured coupling constants.



R = H, C or P

	1”			**2” (A)**					**3” (A)**				**1**	**2**	**3**
	Calculated		Exp.	Calculated				Exp.	Calculated			Exp.	Exp.	Exp.	Exp.
	⇑ [a]	⇓		↓⇑	↑⇑	↑⇓	↑⇓		⇓⇓	⇓⇑	⇑⇑				
10-1	-1.88	-1.79	~1.0	-2.03	-1.98	-1.86	-1.89	0	-1.51	-1.60	-1.64	5.47	6.70	0	0
10-2	9.21	13.48	12.15	8.08	9.31	13.42	13.74	12.60	13.46	11.16	7.64	11.07	18.30	11.55	14.92
10-3	131.94	150.48	187.95	139.57	132.12	132.92	145.37	124.55	131.79	133.13	145.73	188.90	173.80	162.75	174.22
10-4	8.50	2.63	8.25	8.04	9.02	3.23	3.12	9.10	4.50	6.92	9.46	8.92	~1	7.50	6.97
10-5	9.04	7.79	11.40	8.26	7.83	6.47	6.53	11.80	6.68	7.46	9.00	10.20	10.90	9.37	9.45
10-6	2.46 $^5J_{HP}$	2.59 $^5J_{HP}$	2.39 $^5J_{HP}$	2.16 $^5J_{HP}$	2.31 $^5J_{HP}$	2.21 $^5J_{HP}$	2.45 $^5J_{HP}$	1.89 $^5J_{HP}$	2.35	2.48	2.48	2.32 $^5J_{HP}$	bs	bs	>1 $^5J_{HP}$
10-7	4.98 $^3J_{HP}$	6.09 $^3J_{HP}$	6.40 $^3J_{HP}$	4.84 $^3J_{HP}$	4.58 $^3J_{HP}$	5.45 $^3J_{HP}$	5.55 $^3J_{HP}$	6.39 $^3J_{HP}$	5.48 $^3J_{HP}$	5.71 $^3J_{HP}$	4.72 $^3J_{HP}$	6.39 $^3J_{HP}$	7.92 $^3J_{HP}$	7.51 $^3J_{HP}$	7.73 $^3J_{HP}$
10-8	12.47 $^3J_{HP}$	11.26 $^3J_{HP}$	13.10 $^3J_{HP}$	13.23 $^3J_{HP}$	13.16 $^3J_{HP}$	11.41 $^3J_{HP}$	12.15 $^3J_{HP}$	13.58 $^3J_{HP}$	11.29 $^3J_{HP}$	11.21 $^3J_{HP}$	13.41 $^3J_{HP}$	13.18 $^3J_{HP}$	10.44 $^3J_{HP}$	11.60 $^3J_{HP}$	11.92 $^3J_{HP}$
10-9	3.07 $^4J_{HP}$	2.79 $^4J_{HP}$	3.44 $^4J_{HP}$	-	-	-	-	-	-	3.99 $^4J_{PP}$	6.00 $^4J_{PP}$	-	2.63 $^4J_{HP}$	-	-

6-7	-1.23 $^4J_{HH}$	-1.20 $^4J_{HH}$	1.20 $^4J_{HH}$	-1.27	-1.31	-1.23	-1.29	1.00 $^4J_{HH}$	-1.13	-1.17	-1.21	~1.0 $^4J_{HH}$	~1.0 $^4J_{HH}$	bs $^4J_{HH}$	>1 $^4J_{HH}$
6-8	0.93 $^4J_{HH}$	0.87 $^4J_{HH}$	1.25 $^4J_{HH}$	1.37 $^4J_{HH}$	1.28 $^4J_{HH}$	1.32 $^4J_{HH}$	1.22 $^4J_{HH}$	1.91 $^4J_{HH}$	1.13 $^4J_{HH}$	1.11 $^4J_{HH}$	1.14 $^4J_{HH}$	1.97 $^4J_{HH}$	bs	bs $^4J_{HH}$	1.59 $^4J_{HH}$
6-9	4.89 $^3J_{HH}$	4.81 $^3J_{HH}$	4.90 $^3J_{HH}$	-	-	-	-	-	2.35 $^3J_{HH}$	4.82 $^3J_{HH}$	5.09 $^3J_{HH}$	6.39 $^3J_{HP}$	5.69 $^4J_{HH}$	-	7.73 $^3J_{HP}$
7-8	1.10 $^4J_{HH}$	1.12 $^4J_{HH}$	1.50 $^4J_{HH}$	0.92 $^4J_{HH}$	1.10 $^4J_{HH}$	0.95 $^4J_{HH}$	1.12 $^4J_{HH}$	1.92 $^4J_{HH}$	1.13 $^4J_{HH}$	1.17 $^4J_{HH}$	1.13 $^4J_{HH}$	1.97 $^4J_{HH}$	~1.0 $^4J_{HH}$	bs $^4J_{HH}$	1.59 $^4J_{HH}$
7-9	0.60 $^5J_{HH}$	0.54 $^5J_{HH}$	1.00 $^5J_{HH}$	-	-	-	-	-	2.35 $^5J_{HH}$	2.28 $^5J_{HH}$	2.40 $^5J_{HH}$	2.32 $^5J_{HP}$	>1 $^5J_{HH}$	-	>1 $^5J_{HP}$
8-9	7.64 $^3J_{HH}$	7.76 $^3J_{HH}$	7.80 $^3J_{HH}$	-	-	-	-	-	11.30 $^3J_{HH}$	12.40 $^3J_{HH}$	12.75 $^3J_{HH}$	13.18 $^3J_{HP}$	7.92 $^3J_{HH}$	-	11.92 $^3J_{HP}$

[a] The arrow indicates the direction of the P=O (⇓ or ⇑) or C=O (↑ or ↓) vectors with respect to the N_{py} atom: toward (when pointing down) or out (when pointing up).