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Structural effect in the reductive vinylation/phosphorylation of pyridines with alkyl propiolates and secondary phosphine chalcogenides: protonation *vs.* zwitterion generation

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General. The ^{1}H, ^{13}C, ^{15}N, ^{31}P and ^{77}Se NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometer (400.13, 100.62, 40.56, 161.98 and 76.31 MHz, respectively) in $CDCl_3$ solutions and referenced to HMDS (^{1}H, ^{13}C), $MeNO_2$ (^{15}N), H_3PO_4 (^{31}P) and Me_2Se (^{77}Se). The assignment of signals in ^{1}H spectra was performed using 2D homonuclear correlation methods COSY and NOESY. Resonance signals of ^{13}C were assigned with application of 2D heteronuclear correlation methods HSQC and HMBC. FT-IR spectra were obtained with a Bruker Vertex 70 (for **7a-f**) and Varian 3100 FT-IR (for **9a-c** and **11-13**) spectrometer. Melting points (uncorrected) were measured on a Kofler micro hot-stage apparatus. The C, H, N, S microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The P, Se contents were determined by combustion method. Methyl pyridines **1**, **8**, **10**, alkyl propiolates **2**, **3** and diphenylphosphine oxide **4** are commercial reagents (Alfa Aesar). Bis(2-phenylethyl)phosphine chalcogenides **5**, **6** were prepared from styrene and elemental phosphorus as previously reported.[1]

1-[(E)-2-(alkoxycarbonyl)ethenyl]-4-chalcogenophosphoryl-1,4-dihydropyridines **7a-f**, **9a-c**. A solution of methyl pyridine **1, 8** (1.1 mmol), alkyl propiolate **2**, **3** (1.1 mmol) and secondary phosphine chalcogenide **4-6** (1.0 mmol) in MeCN (3 ml) was stirred under an argon atmosphere at 50-52 °C for 5-9 h (for compounds **7a-f**) or 16-20 h (for compounds **9a-c**). After completion the reaction (^{31}P NMR monitoring), the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (for compounds **7a**,**b, 9a**: SiO_2, benzene/1,4-dioxane, 7:1; for compounds **7c-f, 9b,c**: Al_2O_3, hexane/acetone/chloroform, 14:2:1).

Methyl (E)-3-[4-diphenylphosphoryl-3-methylpyridin-1(4H)-yl]prop-2-enoate **7a**. Yield 340 mg (90%), brown powder, mp 155-156 °C (reprecipitated from CCl_4 to Et_2O). IR spectrum (KBr), ν, cm^{-1}: 1688 (C=O), 1638, 1612 (C=C), 1157 (P=O). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 1.73 (3H, s, Me-C_3), 3.68 (3H, s, OMe), 4.04 (1H, dd, $^{2}J_{PH}$ = 21.0, $^{3}J_{4\text{-}5}$ = 4.9, H-4), 4.73 (1H, ddd, $^{3}J_{5\text{-}6}$ = 7.3, $^{3}J_{5\text{-}4}$ = 4.9, $^{3}J_{PH}$ = 3.4, H-5), 4.91 (1H, d, $^{3}J_{HH}$ = 13.6, =C<u>H</u>CO_2Me),

[1] (*a*) B. A. Trofimov and N. K. Gusarova, *Mendeleev Commun.,* 2009, **19**, 295; (*b*) N. K. Gusarova, M. V. Bogdanova, N. I. Ivanova, N. A. Chernysheva, B. G. Sukhov, L. M. Sinegovskaya, O. N. Kazheva, G. G. Alexandrov, O. A. D'yachenko and B. A. Trofimov, *Synthesis*, 2005, 3103; (*c*) B. G. Sukhov, N. K. Gusarova, N. I. Ivanova, M. V. Bogdanova, O. N. Kazheva, G. G. Alexandrov, O. A. D'yachenko, L. M. Sinegovskaya, S. F. Malysheva and B. A. Trofimov, *J. Struct. Chem.*, 2005, **46**, 1066 (*Zh. Strukt. Khim.*, 2005, **46**, 1109).

6.01 (1H, m, H-2), 6.16 (1H, dd, $^{3}J_{6\text{-}5}$ = 7.3, $^{4}J_{PH}$ = 5.2, H-6), 6.99 (1H, d, $^{3}J_{HH}$ = 13.6, =CHN), 7.49 (6H, m, H*m*, H*p*), 7.83 (4H, m, H*o*). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 20.74 (Me-C_3), 44.49 (d, $^{1}J_{PC}$ = 69.1, C-4), 50.89 (OMe), 90.33 (=<u>C</u>HCO_2Me), 102.12 (C-5), 113.01 (C-3), 123.79 (C-2), 128.06, 128.53 (2 d, $^{3}J_{PC}$ = 11.2, C*m*), 128.27 (d, $^{3}J_{PC}$ = 11.6, C-6), 130.19, 131.46 (2 d, $^{1}J_{PC}$ = 94.6, $^{1}J_{PC}$ = 97.8, C*i*), 131.42, 131.89 (d, $^{2}J_{PC}$ = 8.4, C*o*), 131.94 (C*p*), 143.27 (=CHN), 168.43 (C=O). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -246.8. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 28.5. Found, %: C 69.43; H 5.81; N 3.60; P 8.29. $C_{22}H_{22}NO_3P$. Calculated, %: C 69.65; H 5.84; N 3.69; P 8.16.

Ethyl (E)-3-[4-diphenylphosphoryl-3-methylpyridin-1(4H)-yl]prop-2-enoate **7b**. Yield 299 mg (76%), brown powder, mp 73-74 °C (reprecipitated from benzene to hexane). IR spectrum (KBr), ν, cm^{-1}: 1697, 1691 (C=O), 1611 (C=C), 1180 (P=O). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 1.24 (3H, t, $^{3}J_{HH}$ = 7.2, $OCH_2C\underline{H}_3$), 1.70 (3H, s, Me-C_3), 4.02 (1H, dd, $^{2}J_{PH}$ = 21.0, $^{3}J_{4\text{-}5}$ = 4.6, H-4), 4.12 (2H, q, $^{3}J_{HH}$ = 7.2, $OC\underline{H}_2CH_3$), 4.70 (1H, ddd, $^{3}J_{5\text{-}6}$ = 7.8, $^{3}J_{5\text{-}4}$ = 4.6, $^{3}J_{PH}$ = 2.3, H-5), 4.89 (1H, d, $^{3}J_{HH}$ = 13.6, =CHCO_2Et), 5.99 (1H, m, H-2), 6.13 (1H, dd, $^{3}J_{6\text{-}5}$ = 7.8, $^{4}J_{PH}$ = 5.6, H-6), 6.97 (1H, d, $^{3}J_{HH}$ = 13.6, =CHN), 7.46 (6H, m, H*m*, H*p*), 7.80 (4H, m, H*o*). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 14.31 ($OCH_2\underline{C}H_3$), 22.46 (Me-C_3), 44.39 (d, $^{1}J_{PC}$ = 68.7, C-4), 59.41 ($O\underline{C}H_2CH_3$), 90.81 (=<u>C</u>HCO_2Et), 101.82 (C-5), 112.69 (C-3), 123.79 (C-2), 128.04, 128.49 (2 d, $^{3}J_{PC}$ = 11.2, C*m*), 128.79 (C-6), 129.96, 131.20 (2 d, $^{1}J_{PC}$ = 94.7, $^{1}J_{PC}$ = 97.5, C*i*), 131.35, 131.82 (d, $^{2}J_{PC}$ = 8.4, C*o*), 131.96 (C*p*), 143.06 (=CHN), 167.97 (C=O). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -249.7. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 28.8. Found, %: C 70.47; H 6.16; N 3.59; P 7.69. $C_{23}H_{24}NO_3P$. Calculated, %: C 70.22; H 6.15; N 3.56; P 7.87.

Methyl (E)-3-{4-[bis(2-phenylethyl)thiophosphoryl]-3-methylpyridin-1(4H)-yl}prop-2-enoate **7c**. Yield 316 mg (70%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1699, 1683 (C=O), 1634, 1613 (C=C), 614 (P=S). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 1.97, 2.16 (4H, m, CH_2P), 2.05 (3H, s, Me-C_3), 2.94 (4H, m, CH_2Ph), 3.52 (1H, dd, $^{2}J_{PH}$ = 17.2, $^{3}J_{4\text{-}5}$ = 5.3, H-4), 3.66 (3H, s, OMe), 4.90 (1H, ddd, $^{3}J_{5\text{-}6}$ = 7.1, $^{3}J_{5\text{-}4}$ = 5.3, $^{3}J_{PH}$ = 2.3, H-5), 5.13 (1H, dd, $^{3}J_{HH}$ = 13.7, $^{7}J_{PH}$ = 1.7, =C<u>H</u>CO_2Me), 6.23 (1H, d, $^{4}J_{PH}$ = 3.9, H-2), 6.35 (1H, dd, $^{3}J_{6\text{-}5}$ = 7.1, $^{4}J_{PH}$ = 5.6, H-6), 7.10-7.28 (10H, m, Ph), 7.21 (1H, d, $^{3}J_{HH}$ = 13.7, =CHN). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 21.52 (Me-C_3), 27.96, 28.46 (2 d, $^{2}J_{PC}$ = 2.8, $^{2}J_{PC}$ = 3.2, PhCH_2), 29.51, 29.61 (2 d, $^{1}J_{PC}$ = 44.7, $^{1}J_{PC}$ = 45.1, CH_2P), 45.49 (d, $^{1}J_{PC}$ = 47.3, C-4), 50.89 (OMe), 91.64 (d, $^{6}J_{PC}$ = 2.1, =<u>C</u>HCO_2Me), 101.79 (C-5), 113.68 (C-3), 123.95 (C-2), 126.19, 126.31 (C*p*), 127.97, 128.07 (C*o*), 128.40, 128.46 (C*m*), 128.68 (C-6), 140.50, 140.60 (d, $^{3}J_{PC}$ = 13.8, $^{3}J_{PC}$ = 13.4, C*i*), 143.12 (=CHN), 167.99 (C=O). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -249.6. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 52.7. Found, %: C 68.95; H 6.70; N 3.15; P 6.65; S 7.34. $C_{26}H_{30}NO_2PS$. Calculated, %: C 69.16; H 6.70; N 3.10; P 6.86; S 7.10.

Ethyl (E)-3-{4-[bis(2-phenylethyl)thiophosphoryl]-3-methylpyridin-1(4H)-yl}prop-2-enoate **7d**. Yield 289 mg (62%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1699, 1683 (C=O), 1634, 1614 (C=C), 615 (P=S). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 1.26 (3H, t, $^{3}J_{HH}$ = 7.0, $OCH_2C\underline{H}_3$), 1.99, 2.18 (4H, m, CH_2P), 2.07 (3H, s, Me-C_3), 2.96 (4H, m, PhCH_2), 3.55 (1H, dd, $^{2}J_{PH}$ = 17.2, $^{3}J_{4\text{-}5}$ = 5.3, H-4), 4.15 (2H, q, $^{3}J_{HH}$ = 7.0, $OC\underline{H}_2CH_3$), 4.91 (1H, ddd, $^{3}J_{5\text{-}6}$ = 7.6, $^{3}J_{5\text{-}4}$ = 5.4, $^{3}J_{PH}$ = 2.4, H-5), 5.15 (1H, dd, $^{3}J_{HH}$ = 13.6, $^{7}J_{PH}$ = 1.3, =C<u>H</u>CO_2Me), 6.25 (1H, br d, $^{4}J_{PH}$ = 4.2, H-2), 6.37 (1H, dd, $^{3}J_{6\text{-}5}$ = 7.6, $^{4}J_{PH}$ = 5.4, H-6), 7.12-7.29 (10H, m, Ph), 7.22 (1H, d, $^{3}J_{HH}$ = 13.6, =CHN). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 14.30

($OCH_2\underline{C}H_3$), 21.58 (Me-C_3), 28.02, 28.52 (2 d, $^2J_{PC}$ = 2.0, $^2J_{PC}$ = 2.4, CH_2Ph), 29.58, 29.68 (2 d, $^1J_{PC}$ = 44.7, CH_2P), 45.61 (d, $^1J_{PC}$ = 47.0, C-4), 59.59 ($O\underline{C}H_2CH_3$), 92.25 (d, $^6J_{PC}$ = 1.6, $=\underline{C}HCO_2Et$), 101.70 (C-5), 113.66 (C-3), 124.03 (C-2), 126.25, 126.37 (C_p), 128.04, 128.14 (C_o), 128.46, 128.52 (C_m), 128.79 (C-6), 140.57, 140.68 (d, $^3J_{PC}$ = 13.2, $^3J_{PC}$ = 13.6, C_i), 143.00 (=CHN), 167.63 (C=O). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -249.8. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 52.6. Found, %: C 69.48; H 6.96; N 3.09; P 6.43; S 6.65. $C_{27}H_{32}NO_2PS$. Calculated, %: C 69.65; H 6.93; N 3.01; P 6.65; S 6.89.

Methyl (E)-3-{4-[bis(2-phenylethyl)selenophosphoryl]-3-methylpyridin-1(4H)-yl}prop-2-enoate **7e**. Yield 309 mg (62%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1699, 1683 (C=O), 1634, 1615 (C=C), 484 (P=Se). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 2.09, 2.27 (4H, m, CH_2P), 2.09 (3H, s, Me-C_3), 2.96 (4H, m, $PhCH_2$), 3.66 (1H, dd, $^2J_{PH}$ = 15.1, $^3J_{4\text{-}5}$ = 5.1, H-4), 3.68 (3H, s, OMe), 4.97 (1H, ddd, $^3J_{5\text{-}6}$ = 7.9, $^3J_{5\text{-}4}$ = 5.1, $^3J_{PH}$ = 2.3, H-5), 5.15 (1H, d, $^3J_{HH}$ = 13.8, $=C\underline{H}CO_2Me$), 6.27 (1H, br d, $^4J_{PH}$ = 4.6, H-2), 6.40 (1H, dd, $^3J_{6\text{-}5}$ = 7.9, $^4J_{PH}$ = 5.4, H-6), 7.14-7.27 (10H, m, Ph), 7.23 (1H, d, $^3J_{HH}$ = 13.8, =CHN). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 21.82 (Me-C_3), 29.06, 29.56 (2 d, $^2J_{PC}$ = 1.6, $^2J_{PC}$ = 1.9, $PhCH_2$), 29.20, 29.47 (2 d, $^1J_{PC}$ = 38.3, $^1J_{PC}$ = 37.3, CH_2P), 45.07 (d, $^1J_{PC}$ = 39.2, C-4), 51.09 (OMe), 92.17 (d, $^6J_{PC}$ = 2.3, $=\underline{C}HCO_2Me$), 101.96 (C-5), 113.54 (C-3), 124.48 (C-2), 126.42, 126.52 (C_p), 128.18, 128.27 (C_o), 128.60, 128.64 (C_m), 128.89 (C-6), 140.46, 140.53 (d, $^3J_{PC}$ = 13.6, C_i), 143.23 (=CHN), 168.09 (C=O). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -249.1. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 42.3 (s) (+ d-satellites, $^1J_{PSe}$ = 711.6). ^{77}Se NMR (76.31 MHz, $CDCl_3$), δ, ppm (J, Hz): -359.2 (d, $^1J_{PSe}$ = 711.6). Found, %: C 62.39; H 6.04; N 2.86; P 6.05; Se 15.56. $C_{26}H_{30}NO_2PSe$. Calculated, %: C 62.65; H 6.07; N 2.81; P 6.21; Se 15.84.

Ethyl (E)-3-{4-[bis(2-phenylethyl)selenophosphoryl]-3-methylpyridin-1(4H)-yl}prop-2-enoate **7f**. Yield 323 mg (63%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1698, 1681 (C=O), 1633, 1612 (C=C), 483 (P=Se). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 1.25 (3H, t, $^3J_{HH}$ = 7.1, $OCH_2C\underline{H}_3$), 2.03-2.31 (4H, m, CH_2P), 2.09 (3H, s, Me-C_3), 2.96 (4H, m, $PhCH_2$), 3.66 (1H, dd, $^2J_{PH}$ = 15.4, $^3J_{4\text{-}5}$ = 5.4, H-4), 4.15 (2H, q, $^3J_{HH}$ = 7.1, $O\underline{C}H_2CH_3$), 4.96 (1H, ddd, $^3J_{5\text{-}6}$ = 7.8, $^3J_{5\text{-}4}$ = 5.4, $^3J_{PH}$ = 2.3, H-5), 5.15 (1H, d, $^3J_{HH}$ = 13.8, $=C\underline{H}CO_2Et$), 6.28 (1H, br d, $^4J_{PH}$ = 4.6, H-2), 6.41 (1H, dd, $^3J_{6\text{-}5}$ = 7.8, $^4J_{PH}$ = 5.4, H-6), 7.13-7.27 (10H, m, Ph), 7.22 (1H, d, $^3J_{HH}$ = 13.8, =CHN). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 14.43 ($OCH_2\underline{C}H_3$), 21.85 (Me-C_3), 29.09, 29.61 (2 d, $^2J_{PC}$ = 1.7, $^2J_{PC}$ = 2.1, $PhCH_2$), 29.22, 29.48 (2 d, $^1J_{PC}$ = 38.2, $^1J_{PC}$ = 37.4, CH_2P), 45.15 (d, $^1J_{PC}$ = 39.3, C-4), 59.77 ($O\underline{C}H_2CH_3$), 92.72 (d, $^6J_{PC}$ = 2.3, $=\underline{C}HCO_2Et$), 101.82 (C-5), 113.46 (C-3), 124.51 (C-2), 126.45, 126.56 (C_p), 128.22, 128.31 (C_o), 128.63, 128.67 (C_m), 128.98 (C-6), 140.50, 140.57 (d, $^3J_{PC}$ = 13.6, $^3J_{PC}$ = 14.0, C_i), 143.08 (=CHN), 167.71 (C=O). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -249.4. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 42.2 (s) (+ d-satellites, $^1J_{PSe}$ = 711.1). ^{77}Se NMR (76.31 MHz, $CDCl_3$), δ, ppm (J, Hz): -359.2 (d, $^1J_{PSe}$ = 711.1). Found, %: C 63.06; H 6.24; N 2.68; P 5.85; Se 15.26. $C_{27}H_{32}NO_2PSe$. Calculated, %: C 63.28; H 6.29; N 2.73; P 6.04; Se 15.41.

Methyl (E)-3-[2-benzyl-4-(diphenylphosphoryl)pyridin-1(4H)-yl]prop-2-enoate **9a**. Yield 291 mg (64%), vinous powder, mp 91-92 °C (reprecipitated from CCl_4 to Et_2O). IR spectrum (KBr), ν, cm^{-1}: 1693 (C=O), 1602 (C=C), 1158 (P=O). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 3.51 (2H, s, $C\underline{H}_2Ph$), 3.60 (3H, s, OMe), 4.19 (1H, dt, $^2J_{PH}$ = 21.2, $^3J_{4\text{-}3(5)}$ = 4.5, H-4), 4.80 (1H, m, H-3), 4.86 (1H, d, $^3J_{HH}$ = 13.3, $=C\underline{H}CO_2Me$), 5.08 (1H, m, H-5), 6.29 (1H, dd, $^3J_{6\text{-}5}$ = 8.0, $^4J_{PH}$ = 4.1, H-6), 7.05 (2H, m, H_o, $\underline{Ph}CH_2$), 7.22 (3H, m, $H_{m,p}$, $\underline{Ph}CH_2$), 7.37 (1H, d, $^3J_{HH}$ =

13.3, =CHN), 7.44-7.56 (6H, m, $H_{m,p}$, PhP), 7.33-7.85 (4H, m, H_o, PhP). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 37.66 ($\underline{C}H_2Ph$), 39.28 (d, $^1J_{PC}$ = 70.7, C-4), 50.46 (OMe), 90.90 (=$\underline{C}HCO_2Me$), 101.68 (C-3), 103.82 (d, $^1J_{PC}$ = 5.6, C-5), 126.50 (H_p, $CH_2\underline{Ph}$), 126.82 (d, $^3J_{PC}$ = 8.4, C-6), 127.74 (H_m, $CH_2\underline{Ph}$), 127.96 (d, $^3J_{PC}$ = 10.3, C_m, PhP), 128.26 (H_o, $CH_2\underline{Ph}$), 129.71, 130.08 (2 d, $^1J_{PC}$ = 94.5, $^1J_{PC}$ = 96.8, C_i, PhP), 131.23, 131.47 (d, $^2J_{PC}$ = 8.0, C_o, PhP), 131.62 (C_p, PhP), 135.22 (C_i, CH_2Ph), 138.49 (d, $^3J_{PC}$ = 8.0, C-2), 139.54 (=CHN), 167.95 (C=O). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -251.1. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 27.4. Found, %: C 73.67; H 5.79; N 3.05; P 6.59. $C_{28}H_{26}NO_3P$. Calculated, %: C 73.83; H 5.75; N 3.08; P 6.80.

Methyl (E)-3-{2-benzyl-4-[bis(2-phenylethyl)selenophosphoryl]pyridin-1(4H)-yl}prop-2-enoate **9b**. Yield 374 mg (65%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1677 (C=O), 1614 (C=C), 474 (P=Se). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 2.05-2.33 (4H, m, CH_2P), 2.90-3.02 (4H, m, $PhC\underline{H}_2CH_2P$), 3.52 (1H, m, H-4), 3.54 (3H, s, OMe), 3.56 (2H, s, $C\underline{H}_2Ph$), 4.74 (1H, m, H-3), 4.97 (1H, d, $^3J_{HH}$ = 13.3, =$C\underline{H}CO_2Me$), 5.17 (1H, m, H-5), 6.38 (1H, dd, $^3J_{6\text{-}5}$ = 8.0, $^4J_{PH}$ = 4.8, H-6), 6.98-7.21 (15H, m, Ph), 7.55 (1H, d, $^3J_{HH}$ = 13.3, =CHN). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 28.69, 28.73 (2 d, $^1J_{PC}$ = 38.8, $^1J_{PC}$ = 38.0, CH_2P), 29.10, 29.22 ($Ph\underline{C}H_2CH_2P$), 38.23 ($\underline{C}H_2Ph$), 40.26 (d, $^1J_{PC}$ = 41.5, C-4), 51.12 (OMe), 92.78 (=$\underline{C}HCO_2Me$), 102.25 (d, $^2J_{PC}$ = 6.4, C-3), 104.60 (d, $^2J_{PC}$ = 4.4, C-5), 126.56 (C_p, $\underline{Ph}CH_2CH_2P$), 127.14 (d, $^2J_{PC}$ = 7.6, C-6), 127.31 (C_p, $CH_2\underline{Ph}$), 128.27 (C_o, $\underline{Ph}CH_2CH_2P$), 128.45 (C_m, $CH_2\underline{Ph}$), 128.68, 128.71 (C_m, $\underline{Ph}CH_2CH_2P$), 128.95 (C_o, $CH_2\underline{Ph}$), 135.59 (C_i, $CH_2\underline{Ph}$), 139.22 (d, $^3J_{PC}$ = 8.4, C-2), 139.87 (=CHN), 140.39, 140.51 (d, $^3J_{PC}$ = 13.2, $^3J_{PC}$ = 12.4, C_i, $\underline{Ph}CH_2CH_2P$), 168.22 (=$CH\underline{C}O_2Me$). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -250.9. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 44.3 (s) (+ d-satellites, $^1J_{PSe}$ = 708.0). ^{77}Se NMR (76.31 MHz, $CDCl_3$), δ, ppm (J, Hz): -418.6 (d, $^1J_{PSe}$ = 708.0). Found, %: C 66.72; H 5.92; N 2.38; P 5.15; Se 13.56. $C_{32}H_{34}NO_2PSe$. Calculated, %: C 66.89; H 5.96; N 2.44; P 5.39; Se 13.74.

Ethyl (E)-3-{2-benzyl-4-[bis(2-phenylethyl)selenophosphoryl]pyridin-1(4H)-yl}prop-2-enoate **9c**. Yield 335 mg (57%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1684 (C=O), 1610 (C=C), 475 (P=Se). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 1.12 (3H, t, $^3J_{HH}$ = 7.2, $OCH_2C\underline{H}_3$), 1.93-2.21 (4H, m, CH_2P), 2.77-2.91 (4H, m, $PhC\underline{H}_2CH_2P$), 3.56 (1H, dt, $^2J_{PH}$ = 17.7, $^3J_{4\text{-}3(5)}$ = 4.7, H-4), 3.57 (2H, s, $C\underline{H}_2Ph$), 4.00 (2H, q, $^3J_{HH}$ = 7.2, $OC\underline{H}_2CH_3$), 4.76 (1H, m, H-3), 4.97 (1H, d, $^3J_{HH}$ = 13.4, =$C\underline{H}CO_2Et$), 5.16 (1H, m, H-5), 6.38 (1H, dd, $^3J_{6\text{-}5}$ = 8.0, $^4J_{PH}$ = 4.8, H-6), 6.98-7.21 (15H, m, Ph), 7.52 (1H, d, $^3J_{HH}$ = 13.4, =CHN). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 14.34 ($OCH_2\underline{C}H_3$), 28.58, 28.63 (2 d, $^1J_{PC}$ = 39.0, $^1J_{PC}$ = 38.8, CH_2P), 29.04, 29.17 ($Ph\underline{C}H_2CH_2P$), 38.25 ($\underline{C}H_2Ph$), 40.22 (d, $^1J_{PC}$ = 41.3, C-4), 59.71 ($O\underline{C}H_2CH_3$), 93.20 (=$\underline{C}HCO_2Et$), 102.10 (d, $^2J_{PC}$ = 5.7, C-3), 104.37 (d, $^2J_{PC}$ = 5.7, C-5), 126.52 (C_p, $\underline{Ph}CH_2CH_2P$), 127.12 (d, $^3J_{PC}$ = 8.0, C-6), 127.25 (C_p, $CH_2\underline{Ph}$), 128.24 (C_o, $\underline{Ph}CH_2CH_2P$), 128.37 (C_m, $CH_2\underline{Ph}$), 128.64, 128.67 (C_m, $\underline{Ph}CH_2CH_2P$), 128.91 (C_o, $CH_2\underline{Ph}$), 135.58 (C_i, $CH_2\underline{Ph}$), 139.12 (d, $^3J_{PC}$ = 8.0, C-2), 139.67 (=CHN), 140.33, 140.46 (d, $^3J_{PC}$ = 12.6, $^3J_{PC}$ = 12.2, C_i, $\underline{Ph}CH_2CH_2P$), 167.69 (=$CH\underline{C}O_2Et$). ^{15}N NMR (40.56 MHz, $CDCl_3$), δ, ppm (J, Hz): -251.1. ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 43.7 (s) (+ d-satellites, $^1J_{PSe}$ = 708.8). ^{77}Se NMR (76.31 MHz, $CDCl_3$), δ, ppm (J, Hz): -418.7 (d, $^1J_{PSe}$ = 708.8). Found, %: C 67.49; H 6.12; N 2.21; P 5.05; Se 13.26. $C_{33}H_{36}NO_2PSe$. Calculated, %: C 67.34; H 6.16; N 2.38; P 5.26; Se 13.42.

4-Methylpyridine **10** *in the reaction of phosphine chalcogenides* **5** *or* **6** *with methyl propiolate* **2**. A solution of 4-methylpyridine **10** (1.65 mmol), methyl propiolate **2** (1.65 mmol)

and phosphine chalcogenide **5**, **6** (1.5 mmol) in MeCN (4.5 ml) was stirred under an argon atmosphere at 50-52 ºC for 4 h in case of phosphine sulfide **5** and for 3 h in case of phosphine selenide **6.** After completion of the reaction (^{31}P NMR monitoring), solvent was removed under reduced pressure and the residue was purified by flash chromatography for monoadduct **11** on Al_2O_3 (hexane–acetone–chloroform, 14 : 2 : 1). Compounds **12** and **13** were isolated on silica gel using benzene/Et_2O (7:1) as an eluent.

Methyl (E)-3-[bis(2-phenylethyl)selenophosphoryl]prop-2-enoate **11**. Yield 456 mg (75%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1725 (C=O), 1627 sh, 1606 (C=C), 483 (P=Se). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 2.26-2.41 (4H, m, CH_2P), 2.75-2.85, 2.94-3.05 (4H, m, $PhCH_2$), 3.77 (3H, s, OMe), 6.78 (1H, dd, $^3J_{HH}$ = 16.2, $^2J_{PH}$ = 20.1, =CHP), 7.02 (1H, dd, $^3J_{HH}$ = 16.2, $^3J_{PH}$ = 20.1, =C<u>H</u>CO_2Me), 7.15-7.19, 7.24-7.27 (10H, m, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 28.93 ($PhCH_2$), 33.39 (d, $^1J_{PC}$ = 45.9, CH_2P), 52.27 (OMe), 126.59 (C_p), 128.33 (C_o), 128.63 (C_m), 135.87 (d, $^1J_{PC}$ = 58.2, =CHP), 139.11 (d, $^2J_{PC}$ = 6.4, =<u>C</u>HCO_2Me), 139.82 (d, $^3J_{PC}$ = 14.4, C_i), 164.50 (d, $^3J_{PC}$ = 22.4, =CH<u>C</u>O_2Me). ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 32.1 (s) (+ d-satellites, $^1J_{PSe}$ = 737.1). Found, %: C 58.85; H 5.78; P 7.45; Se 19.26. $C_{20}H_{23}O_2PSe$. Calculated, %: C 59.26; H 5.72; P 7.64; Se 19.48.

Methyl (E)-3-[bis(2-phenylethyl)thiophosphoryl]prop-2-enoate **12**. Yield 183 mg (34%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1726 (C=O), 1624, 1605 (C=C), 604 (P=S). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 2.12-2.23 (4H, m, CH_2P), 2.74-2.84, 2.90-3.04 (4H, m, $PhCH_2$), 3.77 (3H, s, OMe), 6.85 (1H, dd, $^3J_{HH}$ = 16.3, $^2J_{PH}$ = 19.6, =CHP), 7.04 (1H, dd, $^3J_{HH}$ = 16.3, $^3J_{PH}$ = 22.1, =C<u>H</u>CO_2Me), 7.14-7.18, 7.23-7.27 (10H, m, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 28.36 ($PhCH_2$), 34.05 (d, $^1J_{PC}$ = 53.3, CH_2P), 52.36 (OMe), 126.71 (C_p), 128.44 (C_o), 128.79 (C_m), 137.55 (d, $^1J_{PC}$ = 65.8, =CHP), 138.19 (d, $^2J_{PC}$ = 5.3, =<u>C</u>HCO_2Me), 140.26 (d, $^3J_{PC}$ = 14.3, C_i), 164.86 (d, $^3J_{PC}$ = 21.9, =CH<u>C</u>O_2Me). ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 42.1. Found, %: C 66.90; H 6.52; P 8.45; S 9.26. $C_{20}H_{23}O_2PS$. Calculated, %: C 67.02; H 6.47; P 8.64; S 8.95.

Methyl (E)-3-{4-[bis(2-phenylethyl)thiophosphoryl]-4-methylpyridin-1(4H)-yl}prop-2-enoate **13**. Yield 169 mg (25%), waxy substance. IR spectrum (neat), ν, cm^{-1}: 1711 (C=O), 1627, 1608 (C=C), 608 (P=S). ^{1}H NMR (400.13 MHz, $CDCl_3$), δ, ppm (J, Hz): 1.50 (3H, d, $^3J_{PH}$ = 15.1, Me-C_4), 2.04-2.18 (4H, m, CH_2P), 2.83-3.09 (4H, m, CH_2Ph), 3.69 (3H, s, OMe), 4.98 (2H, m, H-3,5), 5.16 (1H, d, $^3J_{HH}$ = 13.6, =C<u>H</u>CO_2Me), 6.35 (2H, m, H-2,6), 7.14-7.28 (10H, m, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$), δ, ppm (J, Hz): 24.94 (Me-C_4), 28.19 (d, $^1J_{PC}$ = 44.7, CH_2P), 28.77 (d, $^2J_{PC}$ = 2.8, $PhCH_2$), 41.06 (d, $^1J_{PC}$ = 50.5, C-4), 50.76 (OMe), 93.84 (=<u>C</u>HCO_2Me), 107.86 (C-3,5), 125.97 (C_p), 126.43 (C-2,6), 127.72 (C_o), 128.81 (C_m), 140.61 (d, $^3J_{PC}$ = 13.6, C_i), 142.89 (=CHN), 167.68 (C=O). ^{31}P NMR (161.98 MHz, $CDCl_3$), δ, ppm (J, Hz): 59.9. Found, %: C 68.92; H 6.62; N 3.05; P 6.61; S 6.95. $C_{26}H_{30}NO_2PS$. Calculated, %: C 69.16; H 6.70; N 3.10; P 6.86; S 7.10.