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Phosphorylation of (1-aryl-1-hydroxymethyl)phosphonates

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The ^{31}P, ^{13}C and ^{1}H NMR spectra were taken on a Bruker Avance-300 instrument operating at 121.5, 75.5 and 300 MHz, respectively. Electrospray high-resolution MS measurements (**ESI-HRMS**) were performed on a Thermo Velos Pro Orbitrap Elite Hybrid Mass spectrometer (Thermo Fisher Scientific, Bremen, Germany). The ionization method was ESI and operated in positive ion mode. The capillary temperature was set at 275°C. Samples were infused into the ESI source MeOH solutions at a flow rate of 3 μl min^{-1}. Resolving power of 60,000 (FWHM) at *m/z* 400. Data acquisition and analysis were accomplished with Xcalibur software version 3.0 (Thermo Fisher Scientific Inc.).

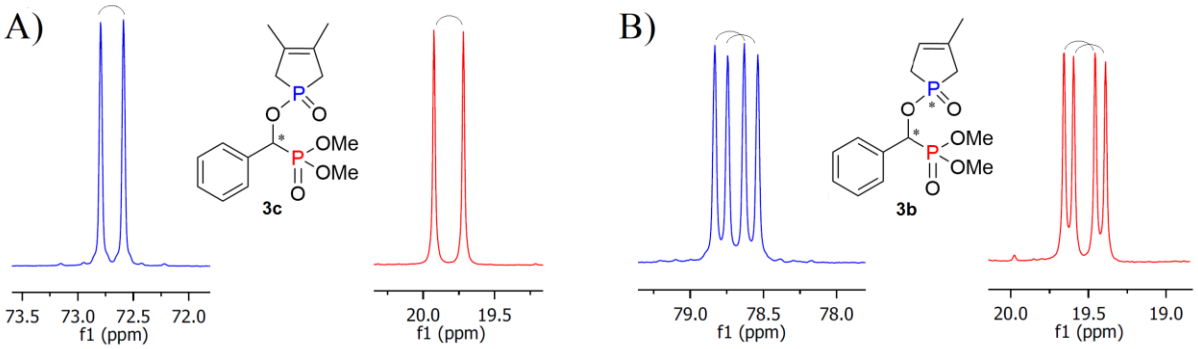

Figure S1 Signals of phosphorus atoms in the $^{31}P\{^{1}H\}$ NMR spectra of compounds **3b,c**.

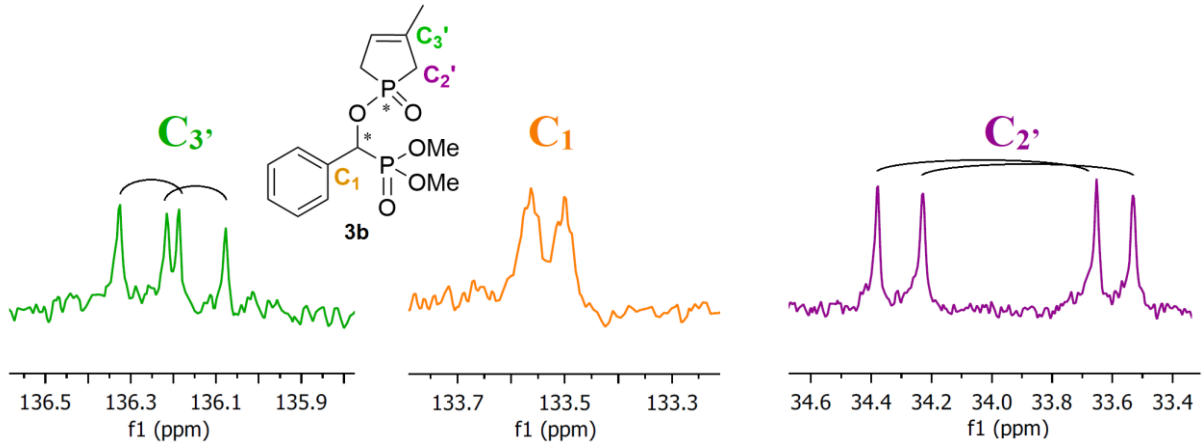

Figure S2 Segments from the ^{13}C NMR spectrum of compound **3b**.

*Dimethyl (1-diphenylphosphoryloxy-1-phenylmethyl)phosphonate (**3a**)*

Yield: 57%, ^{31}P NMR ($CDCl_3$) δ 19.6 (d, ^3J = 25.3, P(O)$(OCH_3)_2$), 35.0 (d, ^3J = 25.3, P(O)Ph_2); ^{13}C NMR ($CDCl_3$) δ 53.7 (d, ^2J = 6.6, OCH_3), 54.0 (d, ^2J = 7.2, OCH_3), 71.4 (dd, ^1J = 172.7, ^2J = 6.8, PCH), 128.1 (d, ^3J = 13.1, $C_{3'}$), 128. 2 (d, ^3J = 6.3, C_2), 128.4 (d, ^4J = 1.9, C_3), 128.5 (d, ^3J = 13.5, $C_{3'}$), 128.9 (d, ^5J = 2.7, C_4), 130.8 (d, ^1J = 137.2, $C_{1'}$), 131.0 (d, ^1J = 138.9, $C_{1'}$), 131.66 (d, ^2J = 10.5, $C_{2'}$), 131.74 (d, ^2J = 10.7, $C_{2'}$), 132.2 (d, ^4J = 2.8, $C_{4'}$), 132.4 (d, ^4J = 2.8, $C_{4'}$), 133.5 (t, ^2J = 1.6, ^3J = 1.6, C_1); ^{1}H NMR ($CDCl_3$) δ 3.57 (d, $^3J_{P,H}$ = 10.6, 3H, OCH_3), 3.69 (d, $^3J_{P,H}$ = 10.7, 3H, OCH_3), 5.70 (dd, $^{2,3}J_{P,H}$ = 11.7, 13.1, 1H, PCH), 7.20-7.64 (m, 13H, Ar), 7.84-7.95 (m, 2H, Ar); $[M+H]^+_{found}$ = 417.10146, $C_{21}H_{23}O_5P_2$ requires 417.10152.

*Dimethyl [1-diphenylphosphoryloxy-1-(4-methylphenyl)methyl]phosphonate (**3b**)*

Yield: 49%, ^{31}P NMR ($CDCl_3$) δ 19.8 (d, ^3J = 25.8, P(O)$(OCH_3)_2$), 34.9 (d, ^3J = 25.8, P(O)Ph_2); ^{13}C NMR ($CDCl_3$) δ 21.2 (CH_3) 53.7 (d, ^2J = 6.6, OCH_3), 54.0 (d, ^2J = 7.2, OCH_3), 71.4 (dd, ^1J = 173.6, ^2J = 6.8, PCH), 128.1 (d, ^3J = 13.3, $C_{3'}$), 128.2 (d, ^3J = 6.5, C_2), 128.5 (d, ^3J = 13.5, $C_{3'}$), 129.1 (d, ^4J = 1.9, C_3), 130.5 (t, ^2J = 1.7, ^3J = 1.7, C_1), 131.0 (d, ^1J = 133.6, $C_{1'}$), 131.2 (d, ^1J = 138.0, $C_{1'}$), 131.7 (d, ^2J = 10.5, $C_{2'}$), 131.8 (d, ^2J = 10.7, $C_{2'}$), 132.1 (d, ^4J = 2.8, $C_{4'}$), 132.4 (d, ^4J = 2.9, $C_{4'}$), 138.8 (d, ^5J = 2.9, C_4); ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 3H, CH_3), 3.57 (d, $^3J_{P,H}$ = 10.5, 3H, OCH_3), 3.69 (d, $^3J_{P,H}$ = 10.7, 3H, OCH_3), 5.66 (dd, $^{2,3}J_{P,H}$ = 11.8, 12.6, 1H, PCH), 7.04-7.09 (m, 2H, Ar), 7.23-7.63 (m, 10H, Ar), 7.85-7.93 (m, 2H, Ar); $[M+H]^+_{found}$ = 431.11669, $C_{22}H_{25}O_5P_2$ requires 431.11717.

*Dimethyl [1-diphenylphosphoryloxy-1-(4-chlorophenyl)methyl]phosphonate (**3c**)*

Yield: 61%, ^{31}P NMR ($CDCl_3$) δ 19.2 (d, ^3J = 25.8, P(O)$(OCH_3)_2$), 35.3 (d, ^3J = 25.8, P(O)Ph_2); ^{13}C NMR ($CDCl_3$) δ 53.7 (d, ^2J = 6.6, OCH_3), 54.1 (d, ^2J = 7.2, OCH_3), 70.7 (dd, ^1J = 173.3, ^2J = 6.8, PCH), 128.3 (d, ^3J = 13.4, $C_{3'}$), 128.55 (d, ^3J = 13.5, $C_{3'}$), 128.59 (d, ^4J = 2.1, C_3), 129.5 (d, ^3J = 6.1, C_2), 130.7 (d, ^1J = 138.6, $C_{1'}$), 131.7 (d, ^2J = 10.6, $C_{2'}$), 132.2 (t, ^2J = 1.6, ^3J = 1.6, C_1), 132.3 (d, ^4J = 2.9, $C_{4'}$), 132.6 (d, ^4J = 2.9, $C_{4'}$), 134.9 (d, ^5J = 3.4, C_4); ^{1}H NMR ($CDCl_3$) δ 3.60 (d, $^3J_{P,H}$ = 10.6, 3H, OCH_3), 3.70 (d, $^3J_{P,H}$ = 10.7, 3H, OCH_3), 5.67 (dd, $^{2,3}J_{P,H}$ = 11.6, 12.9, 1H, PCH), 7.20-7.63 (m, 12H, Ar), 7.84-7.92 (m, 2H, Ar); $[M+H]^+_{found}$ = 451.06232, $C_{21}H_{22}O_5ClP_2$ requires 451.06255.

*Dimethyl [1-diphenylphosphoryloxy-1-(4-nitrophenyl)methyl]phosphonate (**3d**)*

Yield: 70%, ^{31}P NMR ($CDCl_3$) δ 18.3 (d, ^3J = 25.2, P(O)$(OCH_3)_2$), 36.1 (d, ^3J = 25.2, P(O)Ph_2); ^{13}C NMR ($CDCl_3$) δ 53.9 (d, ^2J = 6.7, OCH_3), 54.3 (d, ^2J = 7,2, OCH_3), 70.5 (dd, ^1J = 170.7, ^2J = 6.6, PCH), 123.5 (d, ^4J = 2.2, C_3), 128.5 (d, ^3J = 13.5, $C_{3'}$), 128.7 (d, ^3J = 13.5, $C_{3'}$), 128.8 (d, ^3J = 5.5, C_2), 130.2 (d, ^1J = 137.8, $C_{1'}$), 130.5 (d, ^1J = 134.5, $C_{1'}$), 131.6 (d, ^2J = 10.7, $C_{2'}$), 131.8 (d, ^2J = 10.6, $C_{2'}$), 132.7 (d, ^4J = 2.8, $C_{4'}$), 132.8 (d, ^4J = 2.9, $C_{4'}$), 141.0 (t, ^2J = 1.6, ^3J = 1.6, C_1), 150.0 (d, ^5J = 3.2, C_4); ^{1}H NMR ($CDCl_3$) δ 3.66 (d, $^3J_{P,H}$ = 10.7, 3H, OCH_3), 3.72 (d, $^3J_{P,H}$ = 10.8, 3H, OCH_3), 5.81 (dd, $^{2,3}J_{P,H}$

= 11.2, 14.8, 1H, PCH), 7.25-7.68 (m, 10H, Ar), 7.84-7.96 (m, 2H, Ar), 8.08-8.16 (m, 2H, Ar); $[M+H]^+_{found}$ = 462.08590, $C_{21}H_{22}O_7NP_2$ requires 462.08660.

*Dimethyl [1-(3-methyl-1-oxido-2,5-dihydro-1H-phosphol-1-yloxy)-1-phenylmethyl]phosphonate (**3e**)*

Yield: 59%, ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 3H, $C_{3'}$–CH_3), 1.81 (s, 3H, $C_{3'}$–CH_3), 1.90-2.78 (m, 8H, 4xPCH_2), 3.64 (d, $^3J_{P,H}$ = 10.6, 6H, 2xOCH_3), 3.77 (d, $^3J_{P,H}$ = 10.6, 6H, 2xOCH_3), 5.44 (d, $^3J_{P,H}$ = 35.2, 1H, CH=), 5.55 (d, $^3J_{P,H}$ = 35.4, 1H, CH=), 5.73 (dd, $^{2,3}J_{P,H}$ = 12.3, 12.7, 2H, PCH), 7.27-7.57 (m, 10H, Ar); $[M+H]^+_{found}$ = 331.08555, $C_{14}H_{21}O_5P_2$ requires 331.08587.

Isomer 1: ^{31}P NMR ($CDCl_3$) δ 19.5 (d, ^3J = 25.0, P(O)$(OCH_3)_2$), 78.6 (d, ^3J = 25.0, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 20.7 (d, ^3J = 12.8, $C_{3'}$–*C*H_3), 31.4 (d, ^1J = 87.9, $C_{5'}$), 33.9 (d, ^1J = 87,8, $C_{2'}$), 53.90 (d, ^2J = 6.7, OCH_3), 54.0 (d, ^2J = 7.0, OCH_3), 70.8 (dd, ^1J = 172.4, ^2J = 7.1, PCH), 120.2 (d, ^2J = 11.3, $C_{4'}$), 127.86 (d, ^3J = 5.9, C_2), 128.7-128.8 (m, C_3), 129.1-129.2 (m, C_4), 133.5 (t, ^2J = 1.5, ^3J = 1.5, C_1), 136.2 (d, ^2J = 17.3, $C_{3'}$).

Isomer 2: ^{31}P NMR ($CDCl_3$) δ 19.6 (d, ^3J = 24.4, P(O)$(OCH_3)_2$), 78.7 (d, ^3J = 24.4, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 20.8 (d, ^3J = 13.2, $C_{3'}$–*C*H_3), 31.5 (d, ^1J = 84.4, $C_{5'}$), 34.1 (d, ^1J = 91.4, $C_{2'}$), 53.93 (d, ^2J = 6.6, OCH_3), 54.1 (d, ^2J = 6.9, OCH_3), 70.9 (dd, ^1J = 172.4, ^2J = 6.9, PCH), 120.3 (d, ^2J = 11.2, $C_{4'}$), 127.89 (d, ^3J = 5.8, C_2), 128.7-128.8 (m, C_3), 129.1-129.2 (m, C_4), 133.6 (t, ^2J = 1.5, ^3J = 1.5, C_1), 136.3 (d, ^2J = 17.4, $C_{3'}$).

*Dimethyl [1-(3-methyl-1-oxido-2,5-dihydro-1H-phosphol-1-yloxy)-1-(4-methylphenyl)methyl}-phosphonate (**3f**)*

Yield: 46%, ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 3H, $C_{3'}$–CH_3), 1.80 (s, 3H, $C_{3'}$–CH_3), 1.90-2.76 (m, 8H, 4xPCH_2) overlapped by 2.36 (s, 6H, 2xCH_3), 3.64 (d, $^3J_{P,H}$ = 10.5, 6H, 2xOCH_3), 3.78 (d, $^3J_{P,H}$ = 10.6, 6H, 2xOCH_3), 5.43 (d, $^3J_{P,H}$ = 34.6, 1H, CH=), 5.54 (d, $^3J_{P,H}$ = 36.3, 1H, CH=), 5.72 (dd, $^{2,3}J_{P,H}$ = 11.7, 13.0, 2H, PCH), 7.15-7.46 (m, 8H, Ar); $[M+H]^+_{found}$ = 345.10145, $C_{15}H_{23}O_5P_2$ requires 345.10152.

Isomer 1: ^{31}P NMR ($CDCl_3$) δ 19.9 (d, ^3J = 25.9, P(O)$(OCH_3)_2$), 78.7 (d, ^3J = 25.9, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 20.68 (d, ^3J = 12.9, $C_{3'}$–*C*H_3), 21.3 (CH_3), 31.47 (d, ^1J = 88.0, $C_{5'}$), 34.0 (d, ^1J = 87.9, $C_{2'}$), 53.90 (d, ^2J = 6.7, OCH_3), 54.0 (d, ^2J = 7.2, OCH_3), 70.89 (dd, ^1J = 173.5, ^2J = 7.0, PCH), 120.21 (d, ^2J = 11.2, $C_{4'}$), 127.9 (d, ^3J = 6.0, C_2), 129.5 (d, ^4J = 2.0, C_3), 130.3-130.4 (m, C_1), 136.2 (d, ^2J = 17.3, $C_{3'}$), 139.2 (d, ^5J = 2.9, C_4).

Isomer 2: ^{31}P NMR ($CDCl_3$) δ 20.1 (d, ^3J = 25.5, P(O)$(OCH_3)_2$), 78.8 (d, ^3J = 25.5, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 20.74 (d, ^3J = 13.4, $C_{3'}$–*C*H_3), 21.3 (CH_3), 31.52 (d, ^1J = 84.3, $C_{5'}$), 34.1 (d, ^1J = 91.5, $C_{2'}$), 53.93 (d, ^2J = 6.9, OCH_3), 54.1 (d, ^2J = 7.0, OCH_3), 70.92 (dd, ^1J = 173.6, ^2J = 7.4, PCH), 120.24 (d, ^2J = 11.3, $C_{4'}$), 128.0 (d, ^3J = 6.1, C_2), 129.5 (d, ^4J = 2.0, C_3), 130.3-130.4 (m, C_1), 136.3 (d, ^2J = 17.6, $C_{3'}$), 139.2 (d, ^5J = 2.9, C_4).

*Dimethyl [1-(3-methyl-1-oxido-2,5-dihydro-1H-phosphol-1-yloxy)-1-(4-chlorophenyl)methyl}-phosphonate (**3g**)*

Yield: 54%, ^{1}H NMR ($CDCl_3$) δ 1.72 (s, 3H, $C_{3'}$–CH_3), 1.82 (s, 3H, $C_{3'}$–CH_3), 1.91-2.75 (m, 8H, 4xPCH_2), 3.68 (d, $^{3}J_{P,H}$ = 10.6, 6H, 2xOCH_3), 3.78 (d, $^{3}J_{P,H}$ = 10.7, 6H, 2xOCH_3), 5.46 (d, $^{3}J_{P,H}$ = 36.9, 1H, CH=), 5.56 (d, $^{3}J_{P,H}$ = 37.4, 1H, CH=), 5.73 (dd, $^{2,3}J_{P,H}$ = 12.0, 13.1, 2H, PCH), 7.35-7.51 (m, 8H, Ar); $[M+H]^{+}_{found}$ = 365.04651, $C_{14}H_{20}O_5ClP_2$ requires 365.04690.

Isomer 1: ^{31}P NMR ($CDCl_3$) δ 16.8 (d, ^{3}J = 23.8, P(O)$(OCH_3)_2$), 76.9 (d, ^{3}J = 23.8, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 20.55 (d, ^{3}J = 12.9, $C_{3'}$–*C*H_3), 31.3 (d, ^{1}J = 87.3, $C_{5'}$), 33.86 (d, ^{1}J = 91.0, $C_{2'}$), 53.79 (d, ^{2}J = 6.8, OCH_3), 53.95 (d, ^{2}J = 7.1, OCH_3), 70.02 (dd, ^{1}J = 172.6, ^{2}J = 7.1, PCH), 119.9 (d, ^{2}J = 11.2, $C_{4'}$), 128.8 (d, ^{4}J = 2.1, C_3), 129.01 (d, ^{3}J = 5.9, C_2), 132.1-132.2 (m, C_1), 135.0 (d, ^{5}J = 2.7, C_4), 136.0 (d, ^{2}J = 17.3, $C_{3'}$).

Isomer 2: ^{31}P NMR ($CDCl_3$) δ 16.9 (d, ^{3}J = 23.4, P(O)$(OCH_3)_2$), 77.0 (d, ^{3}J = 23.4, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 20.60 (d, ^{3}J = 13.2, $C_{3'}$–*C*H_3), 31.4 (d, ^{1}J = 84.6, $C_{5'}$), 33.91 (d, ^{1}J = 88.3, $C_{2'}$), 53.82 (d, ^{2}J = 6.8, OCH_3), 54.00 (d, ^{2}J = 7.1, OCH_3), 70.04 (dd, ^{1}J = 173.0, ^{2}J = 7.0, PCH), 120.1 (d, ^{2}J = 11.2, $C_{4'}$), 128.8 (d, ^{4}J = 2.1, C_3), 129.03 (d, ^{3}J = 5.9, C_2), 132.1-132.2 (m, C_1), 135.0 (d, ^{5}J = 2.7, C_4), 136.2 (d, ^{2}J = 17.4, $C_{3'}$).

*Dimethyl [1-(3-methyl-1-oxido-2,5-dihydro-1H-phosphol-1-yloxy)-1-(4-nitrophenyl)methyl}-phosphonate **(3h)***

Yield: 72%, ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 3H, $C_{3'}$–CH_3), 1.85 (s, 3H, $C_{3'}$–CH_3), 2.09-2.80 (m, 8H, 4xPCH_2), 3.72-3.82 (m, 12H, 4xOCH_3), 5.52 (d, $^{3}J_{P,H}$ = 36.9, 1H, CH=), 5.60 (d, $^{3}J_{P,H}$ = 37.5, 1H, CH=), 5.88 (dd, $^{2,3}J_{P,H}$ = 14.2, 11.9, 1H, PCH), 5.89 (dd, $^{2,3}J_{P,H}$ = 14.2, 12.1, 1H, PCH), 7.66-7.72 (m, 4H, $H_{2'}$), 8.24-8.29 (m, 4H, $H_{3'}$); $[M+H]^{+}_{found}$ = 376.07061, $C_{14}H_{20}O_7NP_2$ requires 376.07095.

Isomer 1: ^{31}P NMR ($CDCl_3$) δ 18.39 (d, ^{3}J = 20.6, P(O)$(OCH_3)_2$), 80.3 (d, ^{3}J = 20.6, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 19.7 (d, ^{3}J = 13.0, $C_{3'}$–*C*H_3), 30.4 (d, ^{1}J = 86.7, $C_{5'}$), 32.9 (d, ^{1}J = 90.4, $C_{2'}$), 53.10 (d, ^{2}J = 6.5, OCH_3), 53.2 (d, ^{2}J = 6.3, OCH_3), 68.97 (d, ^{1}J = 169.8, PCH), 118.9 (d, ^{2}J = 11.3, $C_{4'}$), 122.8 (d, ^{4}J = 2.3, C_3), 127.3 (d, ^{3}J = 5.3, C_2), 135.1 (d, ^{2}J = 17.5, $C_{3'}$), 140.1-140.3 (m, C_1), 147.2 (bs, C_4).

Isomer 2: ^{31}P NMR ($CDCl_3$) δ 18.43 (d, ^{3}J = 20.1, P(O)$(OCH_3)_2$), 80.4 (d, ^{3}J = 20.1, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 19.8 (d, ^{3}J = 13.4, $C_{3'}$–*C*H_3), 30.7 (d, ^{1}J = 85.0, $C_{5'}$), 33.2 (d, ^{1}J = 88.7, $C_{2'}$), 53.13 (d, ^{2}J = 6.7, OCH_3), 53.3 (d, ^{2}J = 6.7, OCH_3), 69.03 (d, ^{1}J = 169.5, PCH), 119.4 (d, ^{2}J = 11.4, $C_{4'}$), 122.8 (d, ^{4}J = 2.3, C_3), 127.3 (d, ^{3}J = 5.3, C_2), 135.5 (d, ^{2}J = 17.5, $C_{3'}$), 140.1-140.3 (m, C_1), 147.2 (bs, C_4).

*Dimethyl [1-(3,4-dimethyl-1-oxido-2,5-dihydro-1H-phosphol-1-yloxy)-1-phenylmethyl]phosphonate **(3i)***

Yield: 59%, ^{31}P NMR ($CDCl_3$) δ 19.9 (d, ^{3}J = 25.1, P(O)$(OCH_3)_2$), 72.7 (d, ^{3}J = 25.0, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 16.4 (d, ^{3}J = 15.9, $C_{3'}$–*C*H_3), 16.5 (d, ^{3}J = 16.3, $C_{3'}$–*C*H_3), 36.15 (d, ^{1}J = 86.5, $C_{2'}$), 36.23 (d, ^{1}J = 90.2, $C_{2'}$), 53.8 (d, ^{2}J = 6.7, OCH_3), 54.0 (d, ^{2}J = 7.1, OCH_3), 70.8 (dd, ^{1}J = 172.3, ^{2}J = 7.0, PCH),

127.4 (d, ^{2}J = 13.2, $C_{3'}$), 127.5 (d, ^{2}J = 13.3, $C_{3'}$), 127.8 (d, ^{3}J = 5.9, C_2), 128.7 (d, ^{5}J = 2.2, C_4), 129.1 (d, ^{4}J = 2.8, C_3), 133.6 (t, ^{2}J = 1.6, ^{3}J = 1.6, C_1); ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 3H, $C_{3'}$–CH_3), 1.73 (s, 3H, $C_{3'}$–CH_3), 1.77-2.73 (m, 4H, 2xPCH_2), 3.64 (d, $^{3}J_{P,H}$ = 10.6, 3H, OCH_3), 3.78 (d, $^{3}J_{P,H}$ = 10.6, 3H, OCH_3), 5.73 (dd, $^{2,3}J_{P,H}$ = 11.4, 13.7, 1H, PCH), 7.24-7.58 (m, 5H, Ar); $[M+H]^{+}_{found}$ = 345.10125, $C_{15}H_{23}O_5P_2$ requires 345.10152.

*Dimethyl [1-(3,4-dimethyl-1-oxido-2,5-dihydro-1H-phosphol-1-yloxy)-1-(4-methylphenyl)methyl]-phosphonate (**3j**)*

Yield: 50%, ^{31}P NMR ($CDCl_3$) δ 20.1 (d, ^{3}J = 25.8, $P(O)(OCH_3)_2$), 72.5 (d, ^{3}J = 25.9, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 16.6 (d, ^{3}J = 16.0, $C_{3'}$–*C*H_3), 16.7 (d, ^{3}J = 16.2, $C_{3'}$–*C*H_3), 21.5 (CH_3), 36.4 (d, ^{1}J = 86.5, $C_{2'}$), 36.5 (d, ^{1}J = 90.4, $C_{2'}$), 54.0 (d, ^{2}J = 6.9, OCH_3), 54.2 (d, ^{2}J = 7.0, OCH_3), 70.9 (dd, ^{1}J = 173.3, ^{2}J = 6.8, PCH), 127.6 (d, ^{2}J = 13.1, $C_{3'}$), 128.1 (d, ^{3}J = 6.0, C_2), 129.6 (C_3), 130.7 (C_1), 139.3 (C_4); ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 3H, $C_{3'}$–CH_3), 1.72 (s, 3H, $C_{3'}$–CH_3), 2.01-2.67 (m, 4H, 2xPCH_2) overlapped by 2.36 (s, 3H, CH_3), 3.63 (d, $^{3}J_{P,H}$ = 10.5, 3H, OCH_3), 3.78 (d, $^{3}J_{P,H}$ = 10.6, 3H, OCH_3), 5.69 (dd, $^{2,3}J_{P,H}$ = 11.3, 13.4, 1H, PCH), 7.17-7.22 (m, 2H, H_3), 7.38-7.43 (m, 2H, H_2); $[M+H]^{+}_{found}$ = 359.11697, $C_{16}H_{25}O_5P_2$ requires 359.11717.

*Dimethyl [1-(3,4-dimethyl-1-oxido-2,5-dihydro-1H-phosphol-1-yloxy)-1-(4-chlorophenyl)methyl]-phosphonate (**3k**)*

Yield: 51%, ^{31}P NMR ($CDCl_3$) δ 21.5 (d, ^{3}J = 24.1, $P(O)(OCH_3)_2$), 75.3 (d, ^{3}J = 25.5, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 16.4 (d, ^{3}J = 15.9, $C_{3'}$–*C*H_3), 16.5 (d, ^{3}J = 16.2, $C_{3'}$–*C*H_3), 36.2 (d, ^{1}J = 89.7, $C_{2'}$), 36.3 (d, ^{1}J = 86.8, $C_{2'}$), 53.9 (d, ^{2}J = 6.7, OCH_3), 54.1 (d, ^{2}J = 7.1, OCH_3), 70.1 (dd, ^{1}J = 172.6, ^{2}J = 7.0, PCH), 127.3 (d, ^{2}J = 13.2, $C_{3'}$), 127.5 (d, ^{2}J = 13.3, $C_{3'}$), 128.9 (d, ^{4}J = 2.3, C_3), 129.2 (d, ^{3}J = 5.9, C_2), 133.6 (m, C_1), 135.1 (d, ^{5}J = 3.5, C_4); ^{1}H NMR ($CDCl_3$) δ 1.64 (s, 3H, $C_{3'}$–CH_3), 1.74 (s, 3H, $C_{3'}$–CH_3), 1.05-2.68 (m, 4H, 2xPCH_2), 3.67 (d, $^{3}J_{P,H}$ = 10.6, 3H, OCH_3), 3.78 (d, $^{3}J_{P,H}$ = 10.6, 3H, OCH_3), 5.71 (dd, $^{2,3}J_{P,H}$ = 11.5, 13.7, 1H, PCH), 7.34-7.40 (m, 2H, H_3), 7.43-7.48 (m, 2H, H_2); $[M+H]^{+}_{found}$ = 379.06235, $C_{15}H_{22}O_5ClP_2$ requires 379.06255.

*Dimethyl [1-(3,4-dimethyl-1-oxido-2,5-dihydro-1H-phosphol-1-yloxy)-1-(4-nitrophenyl)methyl]-phosphonate (**3l**)*

Yield: 80%, ^{31}P NMR ($CDCl_3$) δ 16.1 (d, ^{3}J = 24.1, $P(O)(OCH_3)_2$), 72.1 (d, ^{3}J = 25.5, $P_{1'}$); ^{13}C NMR ($CDCl_3$) δ 16.66 (d, ^{3}J = 16.0, $C_{3'}$–*C*H_3), 16.73 (d, ^{3}J = 16.4, $C_{3'}$–*C*H_3), 36.3 (d, ^{1}J = 88.9, $C_{2'}$), 36.6 (d, ^{1}J = 87.4, $C_{2'}$), 54.3 (d, ^{2}J = 6.7, OCH_3), 54.4 (d, ^{2}J = 7.2, OCH_3), 70.1 (dd, ^{1}J = 169.6, ^{2}J = 6.8, PCH), 123.9 (d, ^{4}J = 2.3, C_3), 127.5 (d, ^{2}J = 13.3, $C_{3'}$), 127.9 (d, ^{4}J = 13.4, $C_{3'}$), 128.5 (d, ^{3}J = 5.3, C_2), 141.4 (m, C_1), 148.3 (d, ^{5}J = 3.5, C_4); ^{1}H NMR ($CDCl_3$) δ 1.68 (s, 3H, $C_{3'}$–CH_3), 1.77 (s, 3H, $C_{3'}$–CH_3), 2.37-2.74 (m, 4H, 2xPCH_2), 3.75 (d, $^{3}J_{P,H}$ = 10.7, 3H, OCH_3), 3.78 (d, $^{3}J_{P,H}$ = 10.8, 3H, OCH_3), 5.87

(dd, $^{2,3}J_{P,H}$ = 11.7, 14.7, 1H, PCH), 7.66-7.71 (m, 2H, H_2), 8.23-8.28 (m, 2H, H_3); $[M+H]^+_{found}$ = 390.08662, $C_{15}H_{22}O_7NP_2$ requires 390.08660.

*Dimethyl (1-diphenoxyphosphoryloxy-1-phenylmethyl]phosphonate (**5a**)*

Yield: 15%, ^{31}P NMR ($CDCl_3$) δ -9.6 (d, ^3J = 35.3, $P(O)(OPh)_2$), 20.3 (d, ^3J = 35.3, $P(O)(OCH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 53.9 (d, ^2J = 6.6, OCH_3), 54.1 (d, ^2J = 7.2, OCH_3), 75.7 (dd, ^1J = 172.7, ^2J = 7.3, PCH), 119.9 (d, ^3J = 4.9, $C_{2'}$), 120.2 (d, ^3J = 4.9, $C_{2'}$), 125.3 (d, ^5J = 1.3, $C_{4'}$), 125.5 (d, ^5J = 1.3, $C_{4'}$), 128.1 (d, ^3J = 6.0, C_2), 128.6 (d, ^4J = 1.8, C_3), 129.3 (d, ^5J = 2.8, C_4), 129.6 ($C_{3'}$), 129.7 ($C_{3'}$), 132.4 (t, ^2J = 1.8, ^3J = 1.8, C_1), 150.1 (d, ^2J = 7.4, $C_{1'}$), 150.4 (d, ^2J = 7.2, $C_{1'}$); ^{1}H NMR ($CDCl_3$) δ 3.57 (d, $^3J_{P,H}$ = 10.6, 3H, OCH_3), 3.65 (d, $^3J_{P,H}$ = 10.7, 3H, OCH_3), 5.77 (dd, $^{2,3}J_{P,H}$ = 13.1, 10.5, 1H, PCH), 6.91-6.95 (m, 2H, Ar), 7.07-7.48 (m, 13H, Ar); $[M+H]^+_{found}$ = 449.09087, $C_{21}H_{23}O_7P_2$ requires 449.09135.

*Dimethyl [1-diphenoxyphosphoryloxy-1-(4-chlorophenyl)methyl]phosphonate (**5b**)*

Yield: 17%, ^{31}P NMR ($CDCl_3$) δ -11.5 (d, ^3J = 34.8, $P(O)(OPh)_2$), 17.9 (d, ^3J = 34.8, $P(O)(OCH_3)_2$); ^{13}C NMR ($CDCl_3$) δ 52.9 (d, ^2J = 6.7, OCH_3), 53.1 (d, ^2J = 7.3, OCH_3), 73.9 (dd, ^1J = 173.1, ^2J = 7.2, PCH), 118.9 (d, ^3J = 4.9, $C_{2'}$), 119.1 (d, ^3J = 4.9, $C_{2'}$), 124.4 (d, ^5J = 1.3, $C_{4'}$), 124.6 (d, ^5J = 1.2, $C_{4'}$), 127.8 (d, ^4J = 1.8, C_3), 128.4 (d, ^3J = 5.9, C_2), 134.3 (d, ^5J = 3.2, C_4), 128.6 ($C_{3'}$), 128.8 ($C_{3'}$), 130.1 (t, ^2J = 1.9, ^3J = 1.9, C_1), 149.0 (d, ^2J = 7.4, $C_{1'}$), 149.3 (d, ^2J = 7.4, $C_{1'}$); ^{1}H NMR ($CDCl_3$) δ 3.60 (d, $^3J_{P,H}$ = 10.7, 3H, OCH_3), 3.67 (d, $^3J_{P,H}$ = 10.7, 3H, OCH_3), 5.73 (dd, $^{2,3}J_{P,H}$ = 13.2, 10.6, 1H, PCH), 6.93-6.98 (m, 2H, Ar), 7.10-7.39 (m, 12H, Ar); $[M+H]^+_{found}$ = 483.05173, $C_{21}H_{22}O_7ClP_2$ requires 483.05238.