Experimental procedures and characterization data.

Entry 1/Product : 1-hydroxy-3-phospholene 1-oxide.
To a stirred solution of diallylphosphinic acid (100 mg, 0.68 mmole, 1 equiv) in dry dichloromethane (34.2 ml, typical concentration 0.02M) was added 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene **1** (29 mg, 0.03 mmole, 0.05 equiv). The reaction mixture was refluxed during 4 hours. The reaction was then concentrated under vacuum. The crude (110 mg) was not further purified. ^{1}H NMR of the crude showed no residual substrate and a quantitative conversion. ^{1}H NMR ($CDCl_3$, 200 MHz) 5.90 (d, 2H, *J*= 33.0 Hz), 2.47 (d, 4H, *J*= 13.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz) 126.80 (d, *J*= 14.5 Hz), 30.15 (d, *J*= 93.0 Hz). ^{31}P NMR ($CDCl_3$, 81 MHz) 76.17 . IR (neat, cm^{-1}) 3393, 3048, 2923, 2857, 2352, 1706, 1644, 1450, 1402, 1240, 1177, 1108, 976, 862, 658, 530. MS (CI/ NH_3) 136 [$(M+NH_4)^+$, 100].

Entry 3/Product : 1-benzyloxy-3,4-dimethyl-3-phospholene 1-oxide.
A solution of bis (2-methylallyl)phosphinic acid benzyl ester (51 mg, 0.19 mmole, 1 equiv) in dichloromethane (9.7 ml) with 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene **1** (8 mg, 9.6 $.10^{-3}$ mmole, 0.05 equiv) was refluxed during 60 hours. The reaction was then concentrated under vacuum. ^{1}H NMR of the crude showed a conversion of 88%. Silica gel chromatography was performed using diethyl ether (Rf= 0.13) and gave 37 mg (81%) of a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) 7.42-7.31 (m, 5H), 5.09 (d, 2H, *J*= 8.8 Hz), 2.43 (m, 4H), 1.71 (br s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz) 136.41 (d, *J*= 5.8 Hz), 128.59, 128.36, 128.36, 127.87, 127.44 (d, *J*= 13.1 Hz), 66.12 (d, *J*= 5,8 Hz), 35.37 (d, *J*= 90.1 Hz), 16.47 (d, *J* = 16.0 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz) 70.65 . MS (CI/NH_3) 254 [$(M+NH_4)^+$, 100], 237 [$(M+H)^+$, 14]. IR (neat, cm^{-1}) 3457, 2917, 1646, 1498, 1451, 1399, 1375, 1242, 1196, 1145, 1003, 868, 735, 699.

Entry 4/Product : 1-benzyloxy-3-phenyl-3-phospholene 1-oxide.
A solution of allyl (2-phenylallyl)phosphinic acid benzyl ester (50 mg, 0.16 mmole, 1 equiv) in dichloromethane (8.0 ml) with 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene **1** (14 mg, 1.6 $.10^{-2}$ mmole, 0.1 equiv) was refluxed during 12 hours. The reaction was then concentrated under vacuum. ^{1}H NMR of the crude showed a quantitative conversion without residual substrate. Silica gel chromatography was performed using hexane/ethyl acetate 2/8 (Rf= 0,24) and gave 42 mg (92%) of a pale yellow oil. ^{1}H NMR ($CDCl_3$, 200 MHz) 7.42-7.28 (m, 10H), 6.27 (d, 1H, *J*= 36.7 Hz), 5.16 (d, 2H, *J*= 9.0 Hz), 2.88-2.64 (m, 4H). ^{13}C NMR ($CDCl_3$, 50 MHz) 138.21, 137.84, 136.15 (d, *J*=10.1 Hz), 128.69, 128.55, 128.18, 128.02, 126.31, 125.30, 120.70 (d, *J* = 10.1 Hz), 66.50 (d, *J* = 5,8 Hz), 31.56 (d, *J* = 87.3 Hz), 30.93 (d, *J* = 92.8 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz) 74.27 . MS (CI/NH_3) 302 [$(M+NH_4)^+$, 100], 285 [$(M+H)^+$, 12]. IR (neat, cm^{-1}) 3456, 3038, 2930, 1683, 1619, 1493, 1453, 1392, 1319, 1240, 1191, 1145, 1009, 884, 848, 810, 748, 702.

Entry 6/Product : 3-methyl-4-phenyl-2,5-dihydro-pyrrole-1-carboxylic acid *tert*-butyl ester.
A solution of (2-methylallyl)-(2-phenylallyl)carbamic acid tert-butyl ester (50 mg, 0.17 mmole, 1 equiv) in dichloromethane (8.7 ml) with 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene **1** (21 mg, 2.4 $.10^{-2}$ mmole, 0.14 equiv) was refluxed during 72 hours. The reaction was then concentrated under vacuum. ^{1}H NMR of the crude show a conversion of 83%. Silica gel chromatography was performed using hexane/ethyl acetate 9/1 (Rf= 0,50 in hexane/ethyl acetate 8/2) and gave 34 mg (76%) of a colorless oil. ^{1}H NMR ($CDCl_3$, 200 MHz) mixture of two rotamers. 7.35-7.25 (m, 5H), 4.50-4.42 (m, 2H), 4.27-4.21 (m, 2H), 1.88 (br s, 3H), 1.51-1.50 (2 s, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz) mixture of two rotamers. 154.17, 134.72, 130.28, 129.57 and 129.38, 128.40, 127.52, 127.23, 79.36, 58.69 and 58.37, 56.17 and 55.88, 28.54, 12.85 . MS (CI/NH_3) 277 [$(M+NH_4)^+$, 100], 260 [$(M+H)^+$, 39]. IR (neat, cm^{-1}) 2976, 2853, 1704, 1478, 1406, 1367, 1338, 1251, 1176, 1120, 891, 764, 700.

Entry 8/Product : 2,2-dimethyl-4,7-dipropyl-4,7-dihydro-[1,3,2]dioxasilepine.
A solution of dimethyl-bis-(1-propylallyloxy)silane (50 mg, 0.20 mmole, 1 equiv) in dichloromethane (9.8 ml) with 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene **1** (8 mg, 9.7 $.10^{-3}$ mmole, 0.05 equiv) was refluxed during 2 hours. The reaction was then concentrated under vacuum. ^{1}H NMR of the crude showed a quantitative conversion. the crude (52 mg) was not further purified. (Rf= 0,35 in hexane/diethyl ether 95/05). ^{1}H NMR (200 MHz, $CDCl_3$) 5.53 (d, 2H, *j*=13.9 Hz) 4.60 (m, 2H), 1.40 (m, 8H), 0.93 (t, 6H), 0.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) mixture of diastereomers ratio 2:3. 134.03, 71.38 and 69.79, 40.50 and 40.08,

18..97 and 18.68, 14.02 and 13.79, -2.57 and –3.34 . MS (CI/NH_3) 246 [$(M+NH_4)^+$, 100], 229 [$(M+H)^+$, 95]. IR (neat, cm^{-1}) 2958, 2929, 2857, 1450, 1258, 1095, 1040, 968, 834, 797.

Entry 9/Product : 2,2-dimethyl-6-phenyl-4-propyl-4,7-dihydro-[1,3,2]dioxasilepine.
A solution of dimethyl-(2-phenylallyloxy)(1-propylallyloxy)silane (50 mg, 0.17 mmole, 1 equiv) in dichloromethane (8.6 ml) with 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene **1** (11 mg, 1.3 $.10^{-2}$ mmole, 0.075 equiv) was refluxed during 24 hours. The reaction was then concentrated under vacuum. ^{1}H NMR of the crude showed a conversion of 90%. The crude (51 mg) was not further purified. (Rf= 0,55 in hexane/diethyl ether 9/1). ^{1}H NMR ($CDCl_3$, 200 MHz) 7.32-7;26 (m, 5H), 5.74 (br s, 1H), 4.87 (d, 1H, *J*=15.9 Hz), 4.79 (m, 1H), 4.71 (d, 1H, *J*=15.9 Hz), 1.61 (m, 4H), 0.96 (t, 3H, *J*=6.9 Hz), 0.26 (s, 3H), 0.25 (s, 3H). ^{13}C NMR 142.22, 141.57, 133.11, 128.30, 127.34, 126.62, 69.28, 64.83, 40.41, 18.81 and 18.60, 13.96 and 13.78, -3.03, –3.22. MS (CI/NH_3) 280 [$(M+NH_4)^+$, 100], 263 [$(M+H)^+$, 19]. IR (neat, cm^{-1}) 2959, 2866, 1454, 1260, 1099, 918, 857, 802, 700.

Entry 11/Product : 3-phenyl-2,5-dihydrofuran.
A solution of (1-allyloxymethylvinyl)benzene (50 mg, 0.29 mmole, 1 equiv) in dichloromethane (14.3 ml) with 1,3-dimesitylimidazol-2-ylidene ruthenium benzylidene **1** (12 mg, 1.4 $.10^{-5}$ mmole, 0.05 equiv) was refluxed during 6 hours. The reaction was then concentrated under vacuum. ^{1}H NMR of the crude showed a conversion of 85%. (Rf=0.25 in hexane/diethyl ether 9/1). ^{1}H NMR ($CDCl_3$, 200 MHz) 7.47-7.20 (m, 5H), 6.16 (quint, *J*=2.1 Hz, 1H) , 4.96 (dd, *J* = 4.2 Hz *J*= 2.2 Hz, 1H), 4.92 (dd, *J*= 4.2 Hz *J*= 2.0 Hz, 1H), 4.80 (dd, *J* = 4.2 Hz *J*= 2.0 Hz, 1H), 4.77 (dd, *J*= 4.4 Hz *J*= 2.2 Hz, 1H). ^{13} C NMR ($CDCl_3$. 75 MHz) 138.50, 132.50, 128.60, 128.00, 125.75, 120.45, 76.75, 75.35. MS (CI/NH_3) 164 [$(M+NH_4)^+$, 100], 147 [$(M+H)^+$, 11].

Entry 1/Substrate : diallylphosphinic acid.
Preparation described in reference 12.

Entry 2/Substrate : bis (2-methylallyl)phosphinic acid.
Preparation described in reference 12.

Entry 3/Substrate : bis (2-methylallyl)phosphinic acid benzyl ester.
Preparation described in reference 12.

Entry 4/Substrate : allyl (2-phenylallyl)phosphinic acid benzyl ester.
Preparation described in reference 12.

Entry 6/Substrate : (2-methylallyl)-(2-phenylallyl)carbamic acid *tert*-butyl ester.
Preparation described in reference 15. ^{1}H NMR ($CDCl_3$, 200 MHz) mixture of two rotamers. 7.44-7.27 (m, 5H), 5.37 and 5.31 (2 br s, 1H), 5.11-5.04 (br s, 1H), 4.86 and 4.76 (2 br s, 2H), 4.33 and 4.21 (2 br s, 2H), 3.80 and 3.68 (2 br s, 2H), 1.69 (s, 3H), 1.45 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) mixture of two rotamers. 155.65, 114.15, 144.00, 141.15, 139.55, 138.90, 128.25, 127.75, 126.40, 113.60, 113.05, 111.60 , 79.70, 51.00, 49.35, 48.55, 28.30, 19.95 . SM (CI/NH_3) 305 [$(M+NH_4)^+$, 33], 288 [$(M+H)^+$, 100]. IR (neat, cm^{-1}) 3082, 2976, 2930, 1698, 1456, 1406, 1366, 1241, 1171, 1123, 898, 780, 703.

Entry 8/Substrate : dimethyl-bis-(1-propylallyloxy)silane.
A mixture of dichlorodimethylsilane (1.2ml, 10 mmoles, 1 equiv), 1-hexen-3-ol (2.4 ml, 20 mmoles, 2 equiv) and triethylamine (4.2 ml, 30 mmoles, 3 equiv) in diethyl ether (50 ml) was refluxed during 2 hours. The reaction was then filtrated and concentrated under vacuum. The residual colorless oil (2.5 g, 98%) was used without further purification. (Rf = 0.58 in hexane/ethyl acetate 95/5). ^{1}H NMR ($CDCl_3$, 200 MHz) 5,82 (ddd, *J*=17.2 Hz *J*= 10,2 Hz *J*= 6,2 Hz, 2H), 5.14 (dd, *J*= 17.2 Hz *J*= 1.8 Hz, 2H), 5.04 (dd, *J*= 10.2 Hz *J*= 1.8 Hz, 2H), 4.21 (q, *J*= 6.2 Hz, 2H), 1.41 (m, 8H), 0.91 (t, *J*= 6.9 Hz, 6H), 0.11 (s, 6H). ^{13} C NMR ($CDCl_3$, 50 MHz) 141.30, 113.75, 73.45, 40.00, 18.45, 14.00, -1.60 . MS (CI/NH_3) 274 [$(M+NH_4)^+$, 100], 257 [$(M+H)^+$, 6]. IR (neat, cm^{-1}) 2960, 2934, 2875, 1466, 1257, 1153, 1095, 1070, 1036, 926, 795.

Entry 9/Substrate : dimethyl-(2-phenylallyloxy)(1-propylallyloxy)silane.

To a solution of dichlorodimethylsilane (1.3 ml, 11 mmoles, 2.2 equiv) in diethyl ether (30 ml) is added dropwise a solution of 2-phenyl-2-propen-1-ol (670 mg, 5 mmoles, 1 equiv) and triethylamine (2.9 ml, 11 mmoles, 2.2 equiv) in diethyl ether (5 ml). The reaction mixture was refluxed during 3 hours. After filtration and evaporation of the solvent, the crude was dissolved in diethyl ether (10 ml). The resulting mixture was treated by a solution of 1-hexen-3-ol (600 µl, 5 mmoles, 1 equiv) and triethylamine (2.9 ml, 11 mmoles, 2.2 equiv) in diethyl ether (12.5 ml). The reaction mixture was again refluxed during 3 hours. After filtration and evaporation of the solvent, the crude was purified by silica gel chromatography using hexane/ethyl acetate 97/3 (Rf = 0.40 in hexane/ethyl acetate 95/5) to provide 725 mg (50%) of a colorless oil. ^{1}H NMR($CDCl_3$, 300 MHz) 7.43-7.29 (m, 5H), 5.84 (ddd, *J*= 16.9 Hz *J* = 10.5 Hz *J*= 6.4 Hz, 1H), 5.44 (m, 1H), 5.39 (m, 1H), 5.16 (d, *J*= 16.9 Hz, 1H), 5.05 (d. *J*= 10,6 Hz, 1H), 4.59 (t, *J*= 1.5 Hz, 2H), 4.25 (q, *J*= 6.4 Hz, 1H), 1.57-1.30 (m, 4H), 0.91 (t, *J*= 7.1 Hz, 3H), 0.18 (s, 3H), 0,17 (s, 3H). ^{13} C NMR ($CDCl_3$, 50 MHz) 146.45, 141.15, 139.00, 128.30, 127.65, 126.05, 113.95, 111.75, 73.65, 63.95, 40.00, 18.55, 14.00, -2.45. IR (neat, cm^{-1}) 3058, 2960, 2932, 2873, 1638, 1496, 1466, 1421, 1402, 1258, 1128, 1083, 1036, 926, 903, 871, 799, 707. MS (CI/NH_3) 308 [$(M+NH_4)^+$, 100], 291 [$(M+H)^+$, 11].

<u>Entry 10/Substrate</u> : dimethyl-bis-(2-phenylallyloxy)silane.

Preparation according to procedure of entry 8. Colorless oil. (Rf= 0.32 in hexane/ethyl acetate 95/5). ^{1}H NMR ($CDCl_3$, 300 MHz) 7.43-7.28 (m, 10H), 5.50-5.31 (m, 4H), 4.60 (t, *J*= 1.1 Hz, 4H), 0.21 (s, 6H). ^{13}C NMR ($CDCl_3$, 50 MHz) 146.45, 138.85, 128.35, 127.70, 126.05, 112.00, 64.15, -3.05 . IR 3058, 3031, 2960, 2930, 2873, 1260, 1126, 1080, 1028, 903, 880, 801, 777, 706 . MS (CI/NH_3) 342 [$(M+NH_4)^+$, 100], 325 [$(M+H)^+$, 15].

<u>Entry 11/Substrate</u> : (1-allyloxymethylvinyl)benzene

Sodium hydride (120 mg of a suspension 60% in oil, 3 mmoles, 1 equiv) was added at 0°C to a stirred solution of allylic alcohol (200 µl, 3 mmoles, 1 equiv) in THF (6 ml). The reaction was allowed to warm up to room temperature and a solution of 3-bromo-2-phenyl-1-propene (600 mg, 3 mmoles, 1 equiv) in THF (3 ml) was added dropwise to the reaction mixture. After 4 hours of stirring, the mixture was hydrolyzed with a saturated solution of ammonium chloride (8 ml) and next extracted with diethyl ether (2*10 ml). The organic layers were dried over magnesium sulfate , filtered and concentrated under vacuum. The residue was purified by silica gel chromatography using hexane/ethyl acetate 95/05 providing a colorless oil (130 mg, 75%) (Rf= 0.45 in hexane/ethyl acetate 95/5). ^{1}H NMR ($CDCl_3$, 200 MHz) 7.54-7.45 (m, 2H), 7.40-7.25 (m, 3H), 5.95 (ddt, *J* = 17.2 Hz. *J*= 10.3 Hz *J* = 5.6 Hz, 1H), 5.54 (d, *J*= 0.6 Hz, 1H) , 5.36 (d, *J*= 0.6 Hz, 1H), 5.38-5,17 (m, 2H) , 4.39 (s, 2H) , 4.06 (dt, *J* = 5.6 Hz *J* =1.3 Hz, 2H). ^{13} C NMR ($CDCl_3$, 50 MHz) 144.25, 138.90, 134.70, 128.35, 127.75, 126.05, 117.15, 114.30, 71.95, 71.05 . MS (CI/NH_3) 192 [$(M+NH_4)^+$, 100], 175 [$(M+H)^+$, 5]. IR (neat, cm^{-1}) 3083, 3059, 2928, 2857, 2362, 1730, 1634, 1496, 1448, 1259, 1125, 1084, 1026, 990, 916, 780, 710.

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