Supplementary Material (ESI) for Chemical Communications

Regioselective palladium-catalysed addition reaction of ethyl phenyl-phosphinate with terminal acetylenes: Ligand- and solvent-dependent regioselectivity

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General Procedures

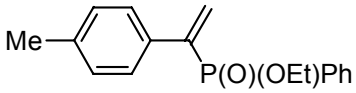
All manipulations involving air and moisture-sensitive compounds were carried out under atmosphere of dry nitrogen, by using standard Schlenk tube techniques. All solvents were distilled over appropriate drying agents prior to use. IR spectra were recorded on a HORIBA FT/IR 730 spectrometer. ^{1}H NMR (300 MHz) and $^{13}C\{^{1}H\}$ NMR (75 MHz) spectra were recorded on a Bruker DPX300 spectrometer at ambient temperature. $^{31}P\{^{1}H\}$ NMR (162 MHz) spectra were recorded on a JEOL JNM-Ex400 spectrometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR chemical shifts were reported in ppm relative to Me_4Si. $^{31}P\{^{1}H\}$ NMR chemical shift was reported in ppm relative to external aq 85% H_3PO_4. High-resolution mass spectra were obtained with a JEOL JMS-700 mass spectrometer at an ionization potential of 70 eV.

Alkynes obtained from commercial source were distilled before use. Ethyl phenylphosphinate, purchased form Aldrich, was distilled before use. Palladium acetate was purchased from Tokyo Kasei, Ltd. and used as received. Phosphines, dppp, dppb (Tokyo Kasei, Ltd), dppe (Wako), dppf and xantphos (Aldrich) were obtained from commercial sources and used as received. $PhPMe_2$ (Aldrich) was distilled before use while *t*-Bu_3P (Strem Chemicals) was used as received.

Synthesis of ethyl (1-phenylethenyl)phenylphosphinate; a representative procedure

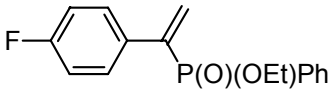
To a mixture of $Pd(OAc)_2$ (0.0148 g, 0.066 mmol) and dppe (1.5 equivalents relative to palladium) in dry toluene (3 mL) under nitrogen were added ethyl phenylphosphinate (0.226 g, 1.33 mmol) and phenylacetylene (0.142 g, 1.39 mmol). The solution was heated at 100 °C for 3 h to produce a transparent yellow solution, which was evaporated. The residue was purified using column chromatography on silica gel (*i*-PrOH/hexane = 1/9) to afford a colourless oil. The major regioisomer **2a** could be separated by Kugelrohr distillation (145 °C/0.226 mm/Hg , 325 mg).

Ethyl [1-(*p*-methylphenyl)ethenyl]phenylphosphinate



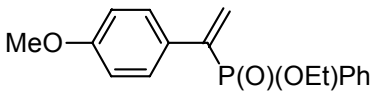
Column chromatography afforded the product ((251.2 mg, 66.1% isolated yield), which was further purified by PTLC (hexane-isopropanol 9:1). Colourless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69-7.76 (m, 2H, Ph-*H*), 7.29-7.46 (m, 5H, Ph-*H*), 7.08 (d, *J*(HH) = 8.3 Hz, 2H, Ph-*H*), 6.27 (dd, 1H, *J*(HH) = 1.5 Hz, *J*(HP) = 19.9 Hz), 6.08 (dd, 1H, *J*(HH) = 1.5 Hz, *J*(HP) = 40.7 Hz), 4.06-4.14 (m, 2H, OCH_2), 2.30 (s, 3H, Ar-CH_3), 1.32 (t, *J*(HH) = 7.1 Hz, 3H, CH_3). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.4. IR (neat, cm^{-1}): 3059, 2981, 1673, 1606, 1510, 1439, 1392, 1278, 1221, 1122, 1034, 955. Anal. calcd for $C_{17}H_{19}O_2P$: C, 71.32; H, 6.69. Found: C, 71.23; H, 6.81. .

Ethyl [1-(*p*-fluorophenyl)ethenyl]phenylphosphinate



Silica gel column chromatography (hexane/isopropanol = 95 : 5) afforded the product (366.6 mg, 72.4 %), which was further purified by PTLC (hexane/isopropanol = 90 : 10). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68-7.73 (m, 2H, Ph-*H*), 7.37-7.47 (m, 5H, Ph-*H*), 6.96 (t, *J*(HH) = 14.6 Hz, 2H, Ph-*H*), 6.23 (dd, 1H, *J*(HH) = 1.1 Hz, *J*(HP) = 20.4 Hz), 6.08 (dd, 1H, *J*(HH) = 1.2 Hz, *J*(HP) = 39.9 Hz), 4.06-4.15 (m, 2H, OCH_2), 1.33 (t, *J*(HH) = 7.1 Hz, 3H, CH_3). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.1. IR (neat, cm^{-1}): 3059, 2985, 2902, 1601, 1508, 1439, 1394, 1223, 1161, 1120, 1028, 955, 843, 800. Anal. calcd for $C_{16}H_{16}FO_2P$: C, 66.20; H, 5.56. Found: C, 66.43; H, 5.67.

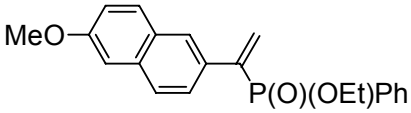
Ethyl [1-(*p*-methoxyphenyl)ethenyl]phenylphosphinate



Silica gel column chromatography (hexane/isopropanol = 96 : 4) afforded the product (0.163 mg; 39.7% isolated yield). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.69-7.76 (m, 2H, Ph-*H*), 7.34-7.42 (m, 5H, Ph-*H*), 6.79 (d, *J*(HH) = 8.7 Hz, 2H, 6.20 (dd, 1H, *J*(HH) = 1.3 Hz, *J*(HP) = 20.0 Hz), 6.08 (dd, 1H, *J*(HH) = 1.3 Hz, *J*(HP) = 41.1

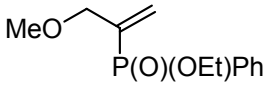
Hz), 4.03-4.18 (m, 2H, OCH_2), 3.76 (s, 3H, OCH_3), 1.33 (t, *J*(HH) = 6.9 Hz, 3H, CH_3). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 32.5. IR (neat, cm^{-1}): 2979, 2902, 2837, 1606, 1510, 1439, 1390, 1296, 1254, 1219, 1180, 1120, 1032, 953, 837. Anal. calcd for $C_{17}H_{19}O_3P$: C, 67.54; H, 6.33. Found: C, 67.56; H, 6.48.

Ethyl [1-(6-methoxy-2-naphthyl)ethenyl]phenylphosphinate



Silica gel column chromatography (hexane/isopropanol = 95 : 5) afforded the product (0.202 mg; 41.3% isolated yield). Colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.62-7.84 (m, 5H, Ar-*H*), 7.36-7.50 (m, 4H, Ar-*H*), 7.07-7.12 (m, 2H, Ar-*H*), 6.32 (d, 1H, *J*(HP) = 21.2 Hz), 6.21 (d, 1H, *J*(HP) = 41.6 Hz), 4.09-4.18 (m, 2H, OCH_2), 3.88 (s, 3H, OCH_3), 1.33 (t, *J*(HH) = 7.0 Hz, 3H, CH_3). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.9. HRMS for $C_{21}H_{21}O_3P$, calcd: 352.1228, found 352.1217.

Ethyl (3-methoxy-1-propen-2-yl)phenylphosphinate



Silica gel column chromatography (hexane/isopropanol = 95 : 5) afforded the product. Gummy liquid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77-7.84 (m, 2H, Ph-*H*), 7.45-7.55 (m, 3H, Ph-*H*), 6.12 (dd, dd, 1H, *J*(HH) = 1.0 Hz, *J*(HP) = 20.0 Hz), 6.08 (dd, 1H, *J*(HH) = 1.0 Hz, *J*(HP) = 42.2 Hz), 4.03-4.14 (m, 4H, OCH_2), 3.28 (s, 3H, OCH_3), 1.36 (t, *J*(HH) = 7.1 Hz, 3H, CH_3). ^{31}P NMR ($CDCl_3$, 162 MHz): δ 31.1. IR (neat, cm^{-1}): 2983, 2931, 2900, 1647, 1508, 1439, 1394, 1228, 1209, 1120, 1034, 955. Anal. calcd for $C_{12}H_{17}O_3P$: C, 59.99; H, 7.13. Found: C, 60.04; H, 6.88.