Supporting Information

for

"Copper-Catalyzed C-P Bond Construction via Direct Coupling of Secondary Phosphines and Phosphites with Aryl and Vinyl Halides"

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General Considerations. Copper (I) iodide (98 %) was purchased from Strem Chemical Company. Cesium carbonate was purchased from Aldrich. Potassium carbonate was purchased from Alfa Aesar. All other reagents are available commercially and were used without further purification. All reagents were weighed and handled in air. Flash column chromatography was performed with Silicycle ultra pure silica gel (230-400 mesh). All reactions were carried out under an argon atmosphere in oven-dried glassware. IR spectra were obtained by placing neat samples directly on the DiComp probe of an ASI REACTIR *in situ* IR instrument. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL 300, Varian XL 500, or Bruker 400 MHz with chemical shifts reported in ppm relative to the residual deuterated solvent, the internal standard tetramethylsilane, or external 85% H_3PO_4 for ^{31}P. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. Gas chromatography analyses were performed on a Hewlett Packard 5890 instrument with a FID detector and a Hewlett Packard 25 m x 0.2 mm i.d. HP-5 capillary column or a Hewlett Packard 6890 instrument with a FID detector and a Hewlett Packard 10 m x 0.1 mm i.d. HP-1 column. Yields refer to isolated yields of compounds greater than 95% purity as determined by capillary gas chromatography (GC), and proton Nuclear Magentic Resonance spectroscopy (^{1}H NMR) analysis. Yields reported in Tables 1 to 2 are an average of two or more runs. The procedures described in this section are representative; thus, the yields may differ slightly from those given in Tables 1 to 2. The CAS number of the known compound was listed. Spectroscopy data of the known compounds matches with the data reported in the corresponding references. All new compounds were further characterized by elemental analysis or HRMS.

General procedure for phosphination of aryl iodides with diarylphosphines (Conditions A). An oven-dried Schlenk tube was evacuated and refilled with argon three times and then charged with CuI (7.8 mg, 0.041 mmol, 5 mol%) followed by anhydrous toluene and diarylphosphine (0.98 mmol). The colorless solution was stirred for 5-10 min. Then the aryl halide (0.82 mmol) and Cs_2CO_3 (513 mg, 1.64 mmol) were added at once followed by anhydrous toluene (1.15 mL). The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C untill the complete conversion of aryl halide. The resulting

suspension was allowed to reach room temperature, diluted with water (2 mL) and extracted with diethyl ether (4 × 4 mL). The combined organic phases were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography on silica with ethyl acetate/hexane to provide the desired product.

Compounds which were prepared using this procedure:

1-Naphthalenyldiphenylphosphane (CAS # 1162-90-9).[1]

(2-Bromophenyl)diphenylphosphane: Additional recrystallization from methanol was required to provide the sample of the analytically pure product, reported yield was based on the analytivally pure product after recrystalization. (CAS # 62336-24-7).[2]

General procedure for phosphination of aryl and vinyl halides with secondary phosphines (Conditions B). An oven-dried Schlenk tube was evacuated and refilled with argon three times and then charged with CuI (7.8 mg, 0.041 mmol, 5 mol%) followed by anhydrous toluene, diaryl or dialkyl phosphines (0.82 mmol) and *N,N'*-dimethylethylenediamine (30 μL, 0.287 mmol, 35 mol%)[*]. The colorless or slightly yellow solution was stirred for 5-10 min. Then the aryl or vinyl halide (0.82 mmol) and Cs_2CO_3 (513 mg, 1.64 mmol)[*] were added at once followed by anhydrous toluene (1.15 mL). The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for the complete conversion of starting material. The resulting suspension was allowed to reach room temperature, diluted with water (2 mL) and extracted with ethyl acetate (4 × 4 mL). The combined organic phases were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography on silica with ethyl acetate/hexane to provide the desired product.

[*] 1.5 equivalents of Cs_2CO_3 (385 mg, 1.23 mmol) and 25 mol% (21 μL, 0.205 mmol) of the ligand were used for the reaction with vinyl iodides.

Compounds which were prepared using this procedure:

(2-Methoxyphenyl)diphenylphosphane. (CAS # 53111-20-9)[3]

(2-Aminophenyl)diphenylphosphane. (CAS # 65423-44-1).[2]

4-(Methoxycarbonyl)phenyldiphenylphosphane. (CAS # 5032-51-9)[4]

3-Diphenylphosphanylpyridine. (CAS # 104114-99-0).[5]

2-Biphenylyldiphenylphosphane (CAS # 13885-09-1).[6]

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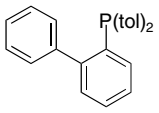
[1] Horner, L.; Simons, G. *Phosphorus and Sulfur and the Related Elements* **1983**, *14*, 189.
[2] Stadler, A.; Kappe, C. O. *Org. Lett.* **2002**, *4*, 3541.
[3] Kwong, F. Y.; Lai, C. W.; Chan, K. S. *Tetrahedron Lett.* **2002**, *43*, 3537.
[4] Kwong, F. Y.; Chan, K. S.; *Chem Comm.* **2000**, *12*, 1069.
[5] Budnikova, Y. G.; Kargin, Y. M.; Sinyashin, O. G. *Russ. J. Gen. Chem.* **2000**, *70*, 524.
[6] Baillie, C.; Chen, W.; Xiao, J. *Tetrahedron Lett.* **2001**, *42*, 9085.



2-Biphenylyldi-p-tolylphosphane. ^{1}H NMR ($CDCl_3$): δ 7.40 (t, J = 7 Hz, 1H), 7.34-7.08 (m, 16H), 2.36 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 148.54 (d, J = 28 Hz), 142.21 (d, J = 6 Hz), 138.70, 136.77 (d, J = 14 Hz), 134,76 (d, J = 10 Hz), 134.46, 134.27 (d, J = 20 Hz), 130.45 (d, J = 5 Hz), 130.12 (d, J = 4 Hz), 129.59 (d, J = 7 Hz), 128.91, 127.93, 127.61 (d, J = 16 Hz), 127.59, 21.74. ^{31}P NMR ($CDCl_3$): δ –14.27. IR (neat): 3008, 1494, 1460, 1186, 803, 752, 698 cm^{-1}. mp. 103-105 °C; $C_{26}H_{23}P$ (366.15) calcd C 85.22, H 6.33, found C 85.11, H 6.43.

(1-Octylvinyl)diphenylphosphane. ^{1}H NMR ($CDCl_3$): δ 7.43-7.36 (m, 10H), 5.64 (dd, J = 20.0, 2.0 Hz, 1H), 4.97 (d, J = 9.0 Hz), 2.16 (q, J = 8.0 Hz, 2H), 1.57-1.49 (m, 2H), 1.32-1.25 (m, 10H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 149.14 (d, J = 28 Hz), 136.19 (d, J = 10 Hz), 134.45 (d, J = 18 Hz), 129.18, 128.72 (d, J = 8 Hz), 123.07 (d, J = 10 Hz), 36.21 (d, J = 22 Hz), 32.27, 29.82, 29.69, 29.64, 29.38 (d, J = 7.0 Hz), 23.08, 14.54. ^{31}P NMR ($CDCl_3$): δ –1.65. IR (neat): 3070, 2955, 3000, 1953, 1889, 1813, 1712, 1465, 1434, 743 cm^{-1}. HRMS (ESI) Calcd for $[M+H]^+$ 325.2080, found 325.2081.

3-(Ethoxycarbonyl)phenyldicyclohexylphosphane, borane complex. ^{1}H NMR ($CDCl_3$): δ 8.38 (d, J = 9 Hz, 1H), 8.18 (d, J = 7 Hz, 1H), 7.96 (t, J = 8 Hz, 1H), 7.56 (t, J = 8 Hz, 1H), 4.43 (q, J = 6 Hz, 2H), 2.13 (q, J = 11 Hz, 2H), 1.97 (d, J = 13 Hz, 2H), 1.84-1.59 (m, 8H), 1.44 (t, J = 6 Hz, 3H), 1.34-1.03 (m, 10H), 1.0-0.0 (br. 3H). ^{13}C NMR ($CDCl_3$): δ 166.42, 138.75 (d, J = 9 Hz), 133.98 (d, J = 6 Hz), 132.41, 131.06 (d, J = 8 Hz), 129.05 (d, J = 8 Hz), 126.80, 61.84, 31.56 (d, J = 33 Hz), 27.12 (d, J = 4 Hz), 27.01 (d, J = 2 Hz), 26.91, 26.63 (d, J = 3 Hz), 26.24, 14.73. ^{31}P NMR ($CDCl_3$): δ 28.73. IR (neat): 3032, 2928, 2370, 1715, 1287, 751 cm^{-1}. mp. 97-98 °C; HRMS (ESI) Calcd for $[M+Na]^+$ 383.2281, found 383.2288.

(4-*t*-Butylphenyl)di-*i*-butylphosphane, borane complex. ^{1}H NMR ($CDCl_3$): δ 7.71-7.68 (m, 2H), 7.47(d, J = 2Hz, 2H), 2.02-1.93 (m, 2H), 1.85-1.73 (m, 4H), 1.34 (s, 9H), 1.01 (2, J = 7 Hz, 6H), 0.79 (d, J = 6 Hz, 6H), 1.0-0.0 (br. 3H). ^{13}C NMR ($CDCl_3$): δ 149.73 (d, J = 5 Hz), 135.60 (d, J = 10 Hz), 131.40 (d, J = 2 Hz), 130.24 (d, J = 8 Hz), 126.02 (d, J = 12 Hz), 124.68 (d, J = 45 Hz), 34.76 (d, J = 32 Hz), 28.52, 27.72, 27.61, 26.42, 27.31, 26.25, 16.52. ^{31}P NMR ($CDCl_3$): δ 11.78. IR (neat): 3050, 2955, 2387, 1463, 1058, 1018 cm^{-1}, mp. 108-110 °C; $C_{18}H_{34}BP$ (292.25) calcd C 73.98, H 11.73, found C 74.05, H 11.85.

2-Biphenyldi-*i*-butylphosphane, borane complex. ^{1}H NMR ($CDCl_3$): δ 8.24 (q, J = 1 Hz, 1H), 7.54-7.44 (m, 5H), 7.33-7.33 (m, 2H), 7.24-7.7.22 (m, 1H), 2.00-1.9 (m, 2H), 1.56-1.45 (m, 2H), 1.37-1.27 (m, 2H), 0.92 (d, J = 7 Hz, 6H), 0.78 (d, J = 6 Hz, 3H), 1.0-0.0 (br. 3H). ^{13}C NMR ($CDCl_3$): δ 146.90, 141.90 (d, J = 2 Hz), 137.09 (d, J = 18 Hz), 132.12 (d, J = 6 Hz), 131.13 (d, J = 3 Hz), 130.99, 128.54, 128.22, 127.91 (d J = 12 Hz), 127.18 (d, J = 43 Hz), 36.18 (d, J = 35 Hz), 25.05, 24.94 (d, J = 8 Hz), 24.67 (d, J = 8 Hz). ^{31}P

NMR ($CDCl_3$): δ 19.03. IR (neat): 3054, 2958, 2383, 1952, 1733, 1464, 1059, 760 cm^{-1}. HRMS (ESI) Calcd for $[M+Na]^+$ 335.2070, found 335.2075.

General procedure for phosphination of aryl iodides with dialkylphosphines. (Conditions C). An oven-dried Schlenk tube was evacuated and refilled with argon three times and then charged with CuI (7.8 mg, 0.041 mmol, 5 mol%) followed by anhydrous toluene, dialkylphosphine (0.82 mmol) and *N,N′*-dimethylethylenediamine (30 μL, 0.287 mmol, 35 mol%). The colorless or slightly yellow solution stirred for 5-10 min. Then the aryl iodide (0.74 mmol) and Cs_2CO_3 (513 mg, 1.64 mmol) were added at once followed by anhydrous toluene (1.15 mL). The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for the desired period of time. The resulting suspension was allowed to reach room temperature and BH_3 in THF (0.9-1.1 mmol) was added at room temperature. The resulting brown suspension stirred for 1-2 h, then diluted with water (2 mL) and extracted with ethyl acetate (4 × 4 mL). The combined organic phases were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography on silica with ethyl acetate/hexane to provide the desired product.

The following compounds were prepared using this procedure:

1-Naphthalenyldicyclohexylphosphane, borane complex. ^{1}H NMR ($CDCl_3$): δ 8.42 (d, J = 8.0 Hz, 1H), 8.22 (q, J = 7.0 Hz, 1H), 8.04 (d, J = 8.0 Hz, 1H), 7.99 (d, J = 8.0 Hz, 1H), 7.68-7.42 (m, 3H), 2.58-2.48 (m, 2H), 2.09 (d, J = 13.0 Hz, 2H), 1.86 (d, J = 10.0 Hz, 2H), 1.66-1.61 (m, 6H), 1.39-1.03 (m, 11H), 1.0-0.0 (br. 3H). ^{13}C NMR ($CDCl_3$): δ 137.11, 134.89, 134.24 (d, J=6 Hz), 130.15, 127.27, 126.40, 125.98, 125,44 (d, J = 10 Hz), 123.85 (d, J = 45 Hz), 34.84 (d, J = 32 Hz), 28.89, 27.59, 27.40 (d, J = 2 Hz), 27.28, 26.16. ^{31}P NMR ($CDCl_3$): δ 31.84. IR (neat): 3054, 2851, 2393, 1506, 1446, 1066, 771 cm^{-1}. mp. 103-105 °C; $C_{22}H_{32}BP$ (338.27) calcd C 78.11, H 9.53, found C 78.27, H 9.63.

(2-Ethylphenyl)dicyclohexylphosphane, borane complex. ^{1}H NMR ($CDCl_3$): δ 7.80 (dd, J = 8.0 Hz, 1H), 7.43 (t, J = 7.0 Hz, 1H), 7.34-7.31 (m, 1H), 7.26 (t, J = 8.0 Hz, 1H), 2.93 (q, J = 8.0 Hz, 2H), 2.21 (q, J = 4.0 Hz, 2H), 1.99 (d, J = 12.0 Hz, 2H), 1.72-1.38 (m, 6H), 1.38-1.16 (m, 10H), 1.29 (t, J = 8.0 Hz, 3H), 1.0-0.0 (br. 3H). ^{13}C NMR ($CDCl_3$): δ 149.73 (d, J = 5 Hz), 135.60 (d, J = 10 Hz), 131.40 (d, J = 2 Hz), 130.24 (d, J = 8 Hz), 126.02 (d, J = 12 Hz), 124.68 (d, J = 45 Hz), 34.76 (d, J = 32 Hz), 28.52, 27.72, 27.61, 26.42, 27.31, 26.25, 16.52. ^{31}P NMR ($CDCl_3$): δ 30.24. IR (neat): 3057, 2931, 2368, 1446, 1064, 757 cm^{-1}. mp. 80-82 °C; HRMS (ESI) Calcd for $[C_{22}H_{34}BP+Na]^+$ 339.2383, found 339.2381.

(4-Cyanophenyl)di-*i*-butylphosphane, borane complex. ^{1}H NMR ($CDCl_3$): δ 7.79 (t, J = 8.0 Hz, 2H), 7.75 (d, J = 7.0 Hz, 2H), 1.99-1.89 (m, 2H), 1.84-1.80 (m, 4H), 1.99 (d, J = 8.0 Hz, 6H), 0.74 (d, J = 8.0 Hz, 6H), 1.0-0.0 (br. 3H). ^{13}C NMR ($CDCl_3$): δ 167.60, 133.99 (d, J = 10 Hz), 132.83 (d, J = 10 Hz), 129.83 (d, J = 50 Hz), 126.57 (d, J = 3 Hz), 34.59 (d, J = 34 Hz), 25.33 (d, J = 8 Hz), 24.89, 24.80 (d, J = 8

Hz). ^{31}P NMR ($CDCl_3$): δ 15.91. IR (neat): 3066, 2956, 2377, 2238, 1462, 1056, 849 cm^{-1}. mp. 93-94 °C; $C_{15}H_{25}BNP$ (261.18) calcd C 68.99, H 9.65, found C 69.04, H 9.69.

General procedure for phosphination of aryl iodides with dialkylphosphines. (Conditions D). An oven-dried Schlenk tube was evacuated and refilled with argon three times and then charged with CuI (7.8 mg, 0.041 mmol, 5 mol%) followed by anhydrous toluene, dialkylphosphine (0.90 mmol) and *N,N′*-dimethylethylenediamine (21 μL, 0.20 mmol, 20 mol%). The colorless or slightly yellow solution was allowed to stir for 5-10 min. Then the aryl iodide (0.82 mmol) and Cs_2CO_3 (513 mg, 1.64 mmol)* were added at once followed by anhydrous toluene (1.15 mL). The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for the desired period of time. The resulting suspension was allowed to reach room temperature and BH_3 in THF (1.1-1.3 mmol) was added at room temperature. The resulting brown suspension was stirred for 1-2 h, then diluted with water (2 mL) and extracted with ethyl acetate (4 × 4 mL). The combined organic phases were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography on silica with ethyl acetate/hexane to provide the desired product.

Compounds which were prepared using this procedure:

(4-Aminophenyl)dicyclohexylphosphane, borane complex. ^{1}H NMR ($CDCl_3$): δ 7.46 (t, J = 9.0 Hz, 2H), 6.73 (d, J = 6.0 Hz, 2H), 3.94 (s, 2H), 2.06-1.60 (m, 12H), 1.35-1.10 (m, 10H), 1.0-0.0 (br. 3H). ^{13}C NMR ($CDCl_3$): δ 149.38, 135.25 (d, J = 8 Hz), 114.98 (d, J = 10 Hz), 112.95 (d, J = 56 Hz), 31.65 (d, J = 35 Hz), 27.24, 27.13, 26.90, 26.54 (d, J = 2 Hz), 26.37. ^{31}P NMR ($CDCl_3$): δ 25.12. IR (neat): 3472, 3374, 3026, 2928, 2370, 1620, 1505 cm^{-1}. mp. 152-153 °C; $C_{18}H_{31}BNP$ (303.23) calcd C 71.30, H 10.03, found C 71.52, H 10.41.

(4-Bromophenyl)dicyclohexylphosphane, borane complex. ^{1}H NMR ($CDCl_3$): δ 7.65-7.55 (m, 4H), 2.11-1.58 (m, 12H), 1.41-1.13 (m, 10H), 1.0-0.0 (br. 3H). ^{13}C NMR ($CDCl_3$): δ 135.32 (d, J = 8 Hz), 132.14 (d, J = 8 Hz), 126.60, 125.19 (d, J = 47 Hz), 31.51 (d, J = 34 Hz), 27.44 (d, J = 4 Hz), 27.02, 26.88, 26.59 (d, J = 2 Hz), 26.24. ^{31}P NMR ($CDCl_3$): δ 28.12. IR (neat): 3056, 2929, 2381, 1574, 1447, 1067, 817, 604 cm^{-1}. mp. 152-153 °C; $C_{18}H_{29}BBrP$ (366.13) calcd C 58.99, H 7.96, found C 58.83, H 8.00.

General procedure for phosphination of aryl and vinyl iodides with dibutylphosphite. An oven-dried Schlenk tube was evacuated and refilled with argon three times and then charged with CuI (10.8 mg, 0.056 mmol, 5 mol%) followed by anhydrous toluene (0.5 mL). *N,N′*-dimethylethylenediamine (35 μL, 0.337 mmol, 30 mol%) and di-*n*-butylphosphite (1.69 mmol) were added under argon and the resulting light blue solution was stirred for 5-10 min. Then aryl or vinyl iodide (1.12 mmol,) and Cs_2CO_3 (725.7 mg, 2.24 mmol) were added at once followed by anhydrous toluene (1.75 mL). The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C* for the the complete consumption of the halides (The reaction progress was monitored by GC). The resulting suspension was allowed to reach room

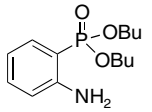
temperature, diluted with water (2 mL) and extracted with diethyl ether (4 × 4 mL). The combined organic phases were dried over $MgSO_4$, concentrated, and the residue was purified by flash chromatography on silica with ethyl acetate/hexane mixture to provide the desired product.

* All reactions using the vinyl iodides were performed at 85 °C.

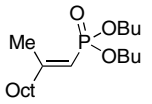
Compounds which were prepared using this procedure:

Dibutyl tolylphosphonate (CAS # 1028-10-0).[7]

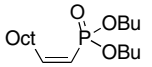
Dibutyl(2-methoxyphenyl)phosphonate (CAS # 128144-50-3).[8]



Dibutyl(2-aminophenyl)phosphonate. ^{1}H NMR ($CDCl_3$): δ 7.45 (dd, J = 6 Hz, 1H), 7.28 (t, J = 7.0 Hz, 1H), 6.74-6.65 (m, 2H), 5.16 (s, 2H), 4.10-3.89 (m, 4H), 1.73-1.63 (m, 4H), 1.48-1.36 (m, 4H), 0.92 (t, J = 8.0 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 151.60 (d, J = 8 Hz), 134.19, 133.59 (d, J = 7 Hz), 117.27 (d, J = 14 Hz), 116.52 (d, J = 14 Hz), 108.40 (d, J = 182 Hz), 66.07 (d, J = 5 Hz), 32.79 (d, J = 7 Hz), 19.15, 14.01. ^{31}P NMR ($CDCl_3$): δ 22.50. IR (neat): 3429, 3336, 3026, 2960, 1800, 1601, 1451, 1221, 1022 cm^{-1}. $C_{14}H_{24}NO_3P$ (285.15) calcd C 58.93, H 8.48, found C 58.87, H 8.67.



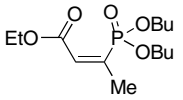
Dibutyl(2-methyldec-1-enyl)phosphonate. ^{1}H NMR ($CDCl_3$): δ 5.38 (d, J = 19.0 Hz, 1H), 3.97 (q, J = 6.0 Hz, 4H), 2.15 (t, J = 7.0 Hz, 2H), 2.08 (d, J = 3.0 Hz, 2H), 1.71-1.62 (m, 4H), 1.46-1.37 (m, 4H), 1.29 (br. 10H), 0.94 (t, J = 7.0 Hz, 6H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 164.71 (d, J = 6 Hz), 111.56 (d, J = 188 Hz), 65.33 (d, J = 6 Hz), 41.88 (d, J = 22 Hz), 32.92 (d, J = 6 Hz), 32.24, 29.79, 29.58 (d, J = 9 Hz), 27.66, 23.06, 20.52 (d, J=7 Hz), 19.22, 14.51, 14.05. ^{31}P NMR ($CDCl_3$): δ 20.07. $C_{19}H_{39}O_3P$ (346.26) calcd C 65.86, H 11.35, found C 65.58, H 11.35.



Dibutyl *cis*-(dec-1-enyl)phosphonate. ^{1}H NMR ($CDCl_3$): δ 6.61-6.34 (m, 1H), 5.58 (dd, J_1=10 Hz, J_2=4 Hz, 1H), 4.03 (q, J=7 Hz, 4H), 2.52 (m, 2H), 1.70-1.63 (m, 4H), 1.46-1.37 (m, 6H), 1.27 (broad, 10H), 0.94 (t, J=7 Hz, 6H), 0.89 (t, J=7 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 154.61 (d, J=5 Hz), 116.64 (d, J=183 Hz), 65.47 (d, J=6 Hz), 32.91 (d, J=6 Hz), 32.25, 31.26 (d, J=8 Hz), 29.84, 29.67 (d, J=5 Hz), 29.38, 23.07, 19.20, 14.51, 14.04. ^{31}P NMR ($CDCl_3$): δ 18.76. IR (neat): 2959, 1624, 1424, 1252, 1024, 977 cm^{-1}. HRMS (ESI) Calcd for $[M+H]^+$ 333.2553, found 333.2575.

[7] Ewdakow, et al. *Zhurnal Obshchei Khimii* (1963), **33**, 3705.

[8] Dawson, N. D.; Burger, A. *Journal of Organic Chemistry* (1953), **18**, 207.

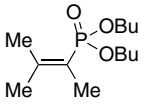


Ethyl 3-(Dibutoxy-phosphoryl)-but-2-enoate. ^{1}H NMR ($CDCl_3$): δ 6.64 (d, J = 20 Hz, 1H), 4.24 (q, J = 7 Hz, 2H), 4.11-3.98 (m, 4H), 2.26 (d, J = 14 Hz, 3H), (m, 2H), 1.71-1.58 (m, 4H), 1.49-1.37 (m, 4H), 1.32 (t, J = 7 Hz, 3H), 0.94 (t, J = 7 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 164.95 (d, J = 31 Hz), 144.16 (d, J = 171 Hz), 130.91 (d, J = 12 Hz), 66.47 (d, J = 6 Hz), 61.02, 32.84 (d, J = 6 Hz), 19.13, 15.09 (d, J = 6 Hz), 14.56, 13.99. ^{31}P NMR ($CDCl_3$): δ 19.22. IR (neat): 2961, 2361, 1723, 1465, 1257, 1063 cm^{-1}. $C_{14}H_{27}O_5P$ (306.16) calcd C 54.89, H 8.88, found C 54.95, H 8.95.

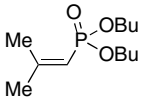
General Procedure for Phosphination of Vinyl Bromides with Dibutylphosphite. An oven-dried Schlenk tube was charged with CuI (10.8 mg, 0.056 mmol, 5 mol%) and Cs_2CO_3 (725.7 mg, 2.24 mmol), briefly evacuated and backfilled with argon. *N,N'*-dimethylethylenediamine (35 μL, 0.337 mmol, 30 mol%) and di-*n*-butylphosphite (1.69 mmol), and vinyl bromide (1.12 mmol,) were added at once followed by anhydrous toluene (1.0 mL). The Schlenk tube was sealed with a Teflon valve and the reaction mixture was stirred at 110 °C for 14 h (The reaction progress was monitored by GC). The reaction mixture was filtered through a silica plug (1×0.5 cm) eluting with ethyl acetate (50 mL). The filtrate was concentrated and the residue was purified by column chromatography on silica gel (hexane-ethyl acetate 1:1) to provide the desired product as a colorless oil.

The following compounds were prepared using this procedure:

Dibutyl prop-2-enylphosphonate: (CAS # 4515423-2).[9]



Dibutyl 3-methylbut-2-enylphosphonate. ^{1}H NMR ($CDCl_3$): δ 4.05-3.91 (m, 4H), 2.15 (dq, J = 3.0, 1.5 Hz, 3H), 1.87-1.80 (m, 6H), 1.71-1.59 (m, 4H), 1.48-1.36 (m, 4H), 1.71-1.58 (m, 4H), 1.49-1.37 (m, 4H), 0.94 (t, J = 7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 150.8 (d, J=12 Hz), 117.7 (d, J=178 Hz), 64.8 (d, J = 6 Hz), 32.6 (d, J = 6.5 Hz), 23.7 (d, J = 7.5 Hz), 22.9 (d, J = 20 Hz), 18.9, 16.5 (d, J=12 Hz), 13.7. ^{31}P NMR ($CDCl_3$): δ 22.7. IR (neat): 2960, 2935, 1632, 1459, 1262, 1225, 1063, 972, 851 cm^{-1}. $C_{13}H_{27}O_3P$ calcd C 59.52, H 10.37, found C 59.22, H 10.38.



Dibutyl 2-methylpropenylphosphonate. ^{1}H NMR ($CDCl_3$): δ 5.39 (dheptat, J = 19.0, 1.0 Hz, 1H), 4.00 (q, J = 6.8 Hz, 4H), 2.11 (dd, J = 4.0, 3.0 Hz, 3H), 1.94 (app t, J = 1.0 Hz, 3H), 1.72-1.61 (m, 4H), 1.49-1.36 (m, 4H), 0.95 (t, J = 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 159.4 (d, J = 24 Hz), 112.2 (d, J = 189 Hz), 65.2 (d, J = 6 Hz), 33.1 (d, J = 6 Hz), 28.2 (d, J = 22 Hz), 21.9 (d, J = 6 Hz), 19.2, 13.9. ^{31}P NMR ($CDCl_3$): δ 20.7.

[9] Hamilton, L. A.; Pitman, N. J. (du Pont de Nemours &Co.). U.S. Patent 2365466; 1942.

IR (neat): 2960, 2937, 2875, 1739, 1638, 1443, 1376, 1245, 1065, 1021, 972, 897 cm^{-1}. $C_{12}H_{25}O_3P$ calcd C 58.05, H 10.15, found C 57.87, H 10.23.