Supporting Information

Palladium-Catalyzed Dehydrogenative Coupling of Terminal Alkynes with Secondary Phosphine Oxides

Jia Yang, Tieqiao Chen, Yongbo Zhou, Shuang-Feng Yin and Li-Biao Han

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China, and National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan

chentieqiao@hnu.edu.cn; libiao-han@aist.go.jp

General information

Reactions for the synthesis of metal intermediates were conducted in a glove box (O₂<0.1 ppm, H₂O<0.1 ppm). All other reactions were carried out in oven-dried Schlenk tubes under N₂ atmosphere. Dry solvents were obtained by purification according to standard methods. Reagents were used as received unless otherwise noted. ¹H NMR, ¹³C NMR and ³¹P NMR data were obtained on a Bruker-400 spectrometer (400 MHz for ¹H, 100 MHz for ¹³C, and 162 MHz for ³¹P NMR spectroscopy). Mass spectra were measured on a Shimadzu GCMS-QP2010 Plus spectrometer (EI). HRMS were conducted in the Analytical Center at Hunan University, China.

General procedure

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\text{Ph} \equiv + \text{Ph} \equiv \xrightarrow{5 \text{ mol}\% \text{Pd(OAc)}_2, \text{2 equiv AgBF}_4, \text{THF, 60}^\circ\text{C, 3 h}} \rightarrow \text{Ph} \equiv \text{P} \equiv \text{P} \equiv \text{Ph}
\]

Under N₂ atmosphere, 0.2 mmol diphenylphosphine oxide, 0.2 mmol phenylacetylene, 5 mol% Pd(OAc)₂, 0.4 mmol AgBF₄ and 0.5 mL THF were charged into a 10 mL schlenck tube, and the mixture was stirred at 60 °C for 3 h. Then 1 mL Et₃N was added. After removal of the volatiles, the residues were passed through a short silica chromatography (particle size 37–54 μm, pether/ethyl acetate as eluent) to afford analytically pure...
alkynylphosphorus compounds 2.

**Characterization data of 2**

2a

Following general procedure (60 °C, 3 h), 2a was isolated as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88–7.94 (m, 4H), 7.43–7.61 (m, 9H), 7.38 (t, 2H, $J = 7.2$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.34; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.06 (d, $J_{P-C} = 121.4$ Hz), 132.56 (d, $J_{P-C} = 1.7$ Hz), 132.28 (d, $J_{P-C} = 2.7$ Hz), 131.00 (d, $J_{P-C} = 11.2$ Hz), 130.74, 128.69 (d, $J_{P-C} = 13.4$ Hz), 128.60, 119.96 (d, $J_{P-C} = 3.9$ Hz), 105.47 (d, $J_{P-C} = 29.8$ Hz), 82.88 (d, $J_{P-C} = 169.4$ Hz). MS (EI): 302.

2b

Following general procedure (60 °C, 6 h), 2b was isolated as a white solid. m.p.: 92–93 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.89–7.95 (m, 4H), 7.48–7.57 (m, 7H), 7.34 (t, 1H, $J = 7.2$ Hz), 7.17–7.27 (m, 2H), 2.47 (s, 3H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.26; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.89 (d, $J_{P-C} = 1.6$ Hz), 133.26 (d, $J_{P-C} = 121.3$ Hz), 133.03 (d, $J_{P-C} = 1.9$ Hz), 132.22 (d, $J_{P-C} = 2.9$ Hz), 130.97 (d, $J_{P-C} = 11.1$ Hz), 130.72, 129.82, 128.66 (d, $J_{P-C} = 13.4$ Hz), 125.84, 119.83 (d, $J_{P-C} = 3.9$ Hz), 104.71 (d, $J_{P-C} = 30.0$ Hz), 86.60 (d, $J_{P-C} = 169.5$ Hz), 20.73. HRMS: Cal.316.1017, Found 316.1011.

2c
Following general procedure (60 °C, 6 h), 2c was isolated as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88–7.93 (m, 4H), 7.47–7.57 (m, 6H), 7.39–7.42 (m, 2H), 7.26–7.27 (m, 2H), 2.35 (s, 3H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.28; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.44, 133.19 (d, $J_{P-C} = 121.4$ Hz), 132.98 (d, $J_{P-C} = 1.9$ Hz), 132.20 (d, $J_{P-C} = 2.9$ Hz), 131.64, 130.99 (d, $J_{P-C} = 11.1$ Hz), 129.69 (d, $J_{P-C} = 1.9$ Hz), 128.65 (d, $J_{P-C} = 13.4$ Hz), 128.49, 119.78 (d, $J_{P-C} = 4.0$ Hz), 105.82 (d, $J_{P-C} = 30.0$ Hz), 82.51 (d, $J_{P-C} = 169.5$ Hz), 21.16. MS (EI): 316.

Following general procedure (60 °C, 6 h), 2d was isolated as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.88–7.93 (m, 4H), 7.47–7.57 (m, 8H), 7.18 (d, $J = 8.0$ Hz), 2.38 (s, 3H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.18; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.40, 133.17 (d, $J_{P-C} = 121.4$ Hz), 132.50 (d, $J_{P-C} = 1.9$ Hz), 132.22 (d, $J_{P-C} = 2.9$ Hz), 131.00 (d, $J_{P-C} = 11.1$ Hz), 129.37, 128.66 (d, $J_{P-C} = 13.4$ Hz), 116.84 (d, $J_{P-C} = 4.1$ Hz), 106.04 (d, $J_{P-C} = 30.3$ Hz), 82.21 (d, $J_{P-C} = 170.7$ Hz), 21.78. MS (EI): 316.

Following general procedure (60 °C, 6 h), 2g was isolated as a white solid. m.p.: 126–127 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87–7.93 (m, 4H), 7.48–7.61 (m, 8H), 7.07 (t, 2H, $J = 8.4$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.34; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 163.88 (d, $J_{F-C} = 252.2$ Hz), 134.82 (dd, $J_{P-C} = 1.9$ Hz, $J_{F-C} = 8.9$ Hz), 132.89 (d, $J_{P-C} = 121.4$ Hz), 132.35 (d, $J_{P-C} = 2.9$ Hz), 130.97 (d, $J_{P-C} = 11.1$ Hz), 128.72 (d, $J_{P-C} = 13.5$ Hz), 116.15 (d, $J_{F-C} = 22.3$ Hz), 104.31 (d, $J_{P-C} = 29.8$ Hz), 82.84 (d, $J_{P-C} = 168.9$ Hz). HRMS: Cal. 320.0766, Found 320.0752.
Following general procedure (60 °C, 18 h), 2h was isolated as a white solid. m.p.: 158–159 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87–7.92 (m, 4H), 7.48–7.58 (m, 8H), 7.35 (d, 2H, $J = 8.4$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.34; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.12, 133.76 (d, $J_{P-C} = 1.8$ Hz), 132.80 (d, $J_{P-C} = 121.6$ Hz), 132.37 (d, $J_{P-C} = 2.9$ Hz), 130.99 (d, $J_{P-C} = 11.2$ Hz), 129.07, 128.73 (d, $J_{P-C} = 13.4$ Hz), 118.43 (d, $J_{P-C} = 4.0$ Hz), 104.05 (d, $J_{P-C} = 24.4$ Hz), 83.98 (d, $J_{P-C} = 166.5$ Hz). HRMS: Cal. 336.0471, Found 336.0454.

Following general procedure (60 °C, 24 h), 2i was isolated as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87–7.92 (m, 4H), 7.44–7.58 (m, 10H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.35; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.86 (d, $J_{P-C} = 1.9$ Hz), 132.73 (d, $J_{P-C} = 121.4$ Hz), 132.42 (d, $J_{P-C} = 2.9$ Hz), 132.00, 130.98 (d, $J_{P-C} = 11.2$ Hz), 128.75 (d, $J_{P-C} = 13.4$ Hz), 125.51, 118.84 (d, $J_{P-C} = 4.0$ Hz), 104.09 (d, $J_{P-C} = 29.2$ Hz), 84.13 (d, $J_{P-C} = 166.3$ Hz). MS (EI): 380.

Following general procedure (60 °C, 6 h), 2j was isolated as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87–7.92 (m, 4H), 7.64–7.73 (m, 4H), 7.50–7.66 (m, 6H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.45; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 132.87 (d, $J_{P-C} = 1.8$ Hz), 132.53 (d, $J_{P-C} = 2.9$ Hz), 132.49 (d, $J_{P-C} = 121.7$ Hz), 132.30 (q, $J_{F-C} = 33.1$ Hz), 131.00 (d, $J_{P-C} = 11.1$ Hz), 128.79 (d, $J_{P-C} = 13.5$ Hz), 125.57 (q, $J_{F-C} = 3.7$ Hz), 123.73 (d, $J_{P-C} = 4.0$ Hz), 123.49 (q, $J_{F-C} = 269.3$ Hz), 103.14 (d, $J_{P-C} = 29.1$ Hz), 85.27 (d, $J_{P-C}$
Following general procedure (60 °C, 18 h), **2k** was isolated as a white solid. m.p.: 151–152 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, 2H, $J$ = 8.4 Hz), 7.88–7.93 (m, 4H), 7.69 (d, 2H, $J$ = 8.4 Hz), 7.49–7.60 (m, 6H), 2.62 (s, 3H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.47; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 196.98, 138.12, 132.75 (d, $J_{P-C}$ = 1.8 Hz), 132.62 (d, $J_{P-C}$ = 121.6 Hz), 132.46 (d, $J_{P-C}$ = 2.9 Hz), 131.00 (d, $J_{P-C}$ = 11.2 Hz), 128.76 (d, $J_{P-C}$ = 13.5 Hz), 128.31, 124.47 (d, $J_{P-C}$ = 3.9 Hz), 103.80 (d, $J_{P-C}$ = 28.7 Hz), 85.82 (d, $J_{P-C}$ = 163.9 Hz), 26.70. HRMS: Cal.344.0966, Found 344.0950.

Following general procedure (60 °C, 24 h), **2l** was isolated as an oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.24 (d, 1H, $J$ = 8.0 Hz), 7.92–8.01 (m, 5H), 7.85 (d, 2H, $J$ = 6.4 Hz), 7.51–7.59 (m, 8H), 7.45 (t, 1H, $J$ = 8.0 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.50; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.36 (d, $J_{P-C}$ = 1.3 Hz), 133.13 (d, $J_{P-C}$ = 121.4 Hz ), 132.98, 132.63 (d, $J_{P-C}$ = 2.1 Hz), 132.37 (d, $J_{P-C}$ = 2.9 Hz), 131.43, 131.05 (d, $J_{P-C}$ = 11.2 Hz), 128.78 (d, $J_{P-C}$ = 13.5 Hz), 128.61, 127.78, 126.98, 125.67, 125.09, 117.43 (d, $J_{P-C}$ = 4.0 Hz), 104.09 (d, $J_{P-C}$ = 29.8 Hz), 87.59 (d, $J_{P-C}$ = 168.0 Hz). MS (EI): 352.

Following general procedure (60 °C, 6 h), **2n** was isolated as a oil. $^1$H NMR (400 MHz,
CDCl₃ δ 7.81–7.87 (m, 4H), 7.43–7.52 (m, 6H), 2.41–2.46 (m, 2H), 1.58–1.65 (m, 2H), 1.38–1.45 (m, 2H), 1.27–1.29 (m, 4H), 0.87 (t, 3H, J = 6.4 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 7.56; ¹³C NMR (100 MHz, CDCl₃) δ 133.38 (d, J_P-C = 121.1 Hz), 132.03 (d, J_P-C = 2.9 Hz), 130.81 (d, J_P-C = 11.2 Hz), 128.51 (d, J_P-C = 13.3 Hz), 109.85 (d, J_P-C = 30.3 Hz), 74.84 (d, J_P-C = 174.2 Hz), 31.11, 28.47, 27.47 (d, J_P-C = 1.6 Hz), 22.43, 19.74 (d, J_P-C = 3.1 Hz), 13.99. HRMS: Cal. 310.1487, Found 310.1475.

Following general procedure (60 °C, 18 h), 2o was isolated as a white solid. m.p.: 143–145 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80–7.85 (m, 4H), 7.44–7.55 (m, 6H), 3.66 (s, 3H), 2.45 (dt, 2H, J = 6.8 Hz, J_P-H = 3.6 Hz), 2.29 (t, 2H, J = 7.6 Hz), 1.57–1.66 (m, 4H), 1.38–1.43 (m, 2H), 1.26–1.31 (m, 6H); ³¹P NMR (162 MHz, CDCl₃) δ 7.54; ¹³C NMR (100 MHz, CDCl₃) δ 174.27, 133.47 (d, J_P-C = 121.1 Hz), 132.03 (d, J_P-C = 2.9 Hz), 130.88 (d, J_P-C = 11.1 Hz), 128.53 (d, J_P-C = 13.4 Hz), 109.72 (d, J_P-C = 30.3 Hz), 74.97 (d, J_P-C = 173.8 Hz), 51.47, 34.05, 29.71, 29.04 (d, J_P-C = 2.1 Hz), 28.79 (d, J_P-C = 0.5 Hz), 27.54 (d, J_P-C = 1.6 Hz), 24.88, 19.78 (d, J_P-C = 3.1 Hz). HRMS: Cal. 396.1854, Found 396.1864.

Following general procedure (60 °C, 24 h), 2p was isolated as a white solid. m.p.: 242–244 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81–7.86 (m, 4H), 7.47–7.54 (m, 6H), 2.47 (b, 2H), 2.34 (t, 2H, J = 6.8 Hz), 1.63 (b, 3H), 1.26–1.45 (m, 10H); ³¹P NMR (162 MHz, CDCl₃) δ 8.50; ¹³C NMR (100 MHz, CDCl₃) δ 177.27, 132.85 (d, J_P-C = 123.3 Hz), 132.22 (d, J_P-C = 2.9 Hz), 130.95 (d, J_P-C = 11.3 Hz), 128.61 (d, J_P-C = 13.4 Hz), 110.24 (d, J_P-C = 30.9 Hz), 74.63 (d, J_P-C = 175.6 Hz), 34.18, 28.29, 28.04, 28.00, 27.92, 27.20 (d, J_P-C = 1.3 Hz), 24.51, 19.82 (d, J_P-C = 3.0 Hz). HRMS: Cal.382.1698, Found
Following general procedure (60 °C, 24 h), 2q was isolated as a white solid. m.p.: 81–82 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73–7.79 (m, 4H), 7.39–7.47 (m, 6H), 2.28 (b, 2H), 1.75(d, 2H, $J = 4.4$ Hz), 1.56–1.66 (m, 3H), 0.95–1.22 (m, 6H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 7.58; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.52 (d, $J_{P-C} = 121.0$ Hz), 132.02 (d, $J_{P-C} = 2.8$ Hz), 130.87 (d, $J_{P-C} = 11.1$ Hz), 128.54 (d, $J_{P-C} = 23.4$ Hz), 108.92 (d, $J_{P-C} = 30.5$ Hz), 75.73 (d, $J_{P-C} = 174.3$ Hz), 36.77, 32.73, 27.52 (d, $J_{P-C} = 3.0$ Hz), 26.02, 25.96. HRMS: Cal. 322.1487, Found 322.1471.

Following general procedure (100 °C, 18 h), 2r was isolated as an oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.73–7.78 (m, 4H), 7.36–7.46 (m, 6H), 2.54–2.59 (m, 1H), 1.78-1.82 (m, 2H), 1.61–1.66 (m, 2H), 1.45–1.55 (m, 3H), 1.24–1.28 (m, 3H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 7.67; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.56 (d, $J_{P-C} = 121.0$ Hz), 131.99 (d, $J_{P-C} = 2.9$ Hz), 130.84 (d, $J_{P-C} = 11.1$ Hz), 128.53 (d, $J_{P-C} = 13.3$ Hz), 113.23 (d, $J_{P-C} = 29.6$ Hz), 74.55 (d, $J_{P-C} = 174.2$ Hz), 31.45 (d, $J_{P-C} = 1.3$ Hz), 29.82 (d, $J_{P-C} = 3.0$ Hz), 25.56, 24.59. HRMS: Cal. 308.1330, Found 308.1314.

Following general procedure (100 °C, 18 h), 2s was isolated as a white solid. m.p.: 130–
131 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79–7.85 (m, 4H), 7.44–7.54 (m, 6H), 1.34 (s, 9H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 7.64; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 133.60 (d, $J_{P-C}$ = 121.0 Hz), 131.97 (d, $J_{P-C}$ = 2.9 Hz), 130.83 (d, $J_{P-C}$ = 11.1 Hz), 128.53 (d, $J_{P-C}$ = 13.3 Hz), 116.79 (d, $J_{P-C}$ = 28.7 Hz), 73.08 (d, $J_{P-C}$ = 173.8 Hz), 29.98 (d, $J_{P-C}$ = 1.5 Hz), 28.51 (d, $J_{P-C}$ = 2.8 Hz). HRMS: Cal. 282.1174, Found 282.1157.

Following general procedure (60 °C, 24 h), 2t was isolated as a white solid. m.p.: 110–111 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (b, 4H), 7.46–7.54 (m, 6H), 6.48 (b, 1H), 2.16–2.20 (m, 4H), 1.59–1.67 (m, 4H); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 8.13; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.70 (d, $J_{P-C}$ = 12.6 Hz), 132.49 (d, $J_{P-C}$ = 121.2 Hz ), 130.94 (d, $J_{P-C}$ = 2.9 Hz ), 129.90 (d, $J_{P-C}$ = 11.1 Hz), 127.53 (d, $J_{P-C}$ = 14.3 Hz), 117.88 (d, $J_{P-C}$ = 4.2 Hz ), 106.81 (d, $J_{P-C}$ = 30.2 Hz ), 79.08 (d, $J_{P-C}$ = 173.2 Hz ), 26.98 (d, $J_{P-C}$ = 1.0 Hz), 24.88, 20.82, 20.05. HRMS: Cal. 306.1174, Found 306.1166.

Following general procedure (60 °C, 24 h), 2u was isolated as an oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54 (d, 2H, $J$ = 7.6 Hz), 7.35–7.46 (m, 3H), 1.89–2.01 (m, 4H), 1.69–1.77 (m, 4H), 1.45–1.54 (m, 4H), 0.97 (t, 6H, $J$ = 7.2 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 26.13; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 132.38 (d, $J_{P-C}$ = 1.7 Hz), 130.34, 128.54, 120.24 (d, $J_{P-C}$ = 3.6 Hz ), 102.42 (d, $J_{P-C}$ = 25.1 Hz), 82.94 (d, $J_{P-C}$ = 143.7 Hz), 31.12 (d, $J_{P-C}$ = 79.6 Hz), 24.03 (d, $J_{P-C}$ = 4.1 Hz), 23.95 (d, $J_{P-C}$ = 15.8 Hz), 13.66. HRMS: Cal. 262.1487, Found 262.1472.
Following general procedure (60 °C, 24 h), 2v was isolated as an oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81–7.86 (m, 2H), 7.29–7.51 (m, 8H), 2.02–2.11 (m, 2H), 1.55–1.65 (m, 2H), 1.33–1.42 (m, 2H), 0.84 (t, 3H, $J = 8.0$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.01; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 132.49 (d, $J_{P-C} = 1.7$ Hz), 132.27 (d, $J_{P-C} = 114.5$ Hz), 132.19 (d, $J_{P-C} = 2.8$ Hz), 130.53 (d, $J_{P-C} = 5.5$ Hz), 130.40, 128.70 (d, $J_{P-C} = 12.8$ Hz), 128.58, 120.07 (d, $J_{P-C} = 3.8$ Hz), 103.75 (d, $J_{P-C} = 27.5$ Hz), 82.86 (d, $J_{P-C} = 156.0$ Hz), 33.67 (d, $J_{P-C} = 83.7$ Hz), 23.90 (d, $J_{P-C} = 2.1$ Hz), 23.84 (d, $J_{P-C} = 24.9$ Hz), 13.62. HRMS: Cal. 282.1174, Found 282.1157.

Following general procedure (60 °C, 24 h), 2w was isolated as an oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81–7.86 (m, 2H), 7.49–7.57 (m, 3H), 2.40 (t, 2H, $J = 7.2$ Hz), 1.97–2.05 (m, 2H), 1.57–1.62 (m, 4H), 1.38–1.43 (m, 4H), 1.30 (b, 4H), 0.89 (t, 6H, $J = 6.8$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 16.38; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 132.59 (d, $J_{P-C} = 114.3$ Hz), 131.88 (d, $J_{P-C} = 2.8$ Hz), 130.30 (d, $J_{P-C} = 10.5$ Hz), 128.47 (d, $J_{P-C} = 12.7$ Hz), 107.83 (d, $J_{P-C} = 28.1$ Hz), 74.69 (d, $J_{P-C} = 161.9$ Hz), 33.67 (d, $J_{P-C} = 84.0$ Hz), 31.10, 28.43, 27.48, 23.85 (d, $J_{P-C} = 9.5$ Hz), 23.73 (d, $J_{P-C} = 22.4$ Hz), 22.41, 19.54 (d, $J_{P-C} = 2.9$ Hz), 13.94, 13.53. HRMS: Cal. 290.1800, Found 290.1782.

Following general procedure (60 °C, 12 h), 2x was isolated as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.54–7.56 (m, 2H), 7.35–7.46 (m, 3H), 2.05–2.08 (m, 2H), 1.86–
1.99 (m, 8H), 1.68–1.76 (m, 2H), 1.49–1.61 (m, 4H), 1.21–1.41 (m, 6H); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 35.75; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.44 (d, $J_{P-C} = 1.6$ Hz), 130.29, 128.52, 120.31 (d, $J_{P-C} = 3.5$ Hz), 103.41 (d, $J_{P-C} = 21.8$ Hz), 81.02 (d, $J_{P-C} = 137.0$ Hz), 36.69 (d, $J_{P-C} = 78.3$ Hz), 26.29 (d, $J_{P-C} = 9.5$ Hz), 26.15 (d, $J_{P-C} = 9.2$ Hz), 25.82 (d, $J_{P-C} = 1.3$ Hz), 25.74 (d, $J_{P-C} = 3.2$ Hz), 24.66 (d, $J_{P-C} = 3.3$ Hz). MS (EI): 314.

Under N$_2$ atmosphere, 0.2 mmol Ph(EtO)P(O)H 1e, 0.2 mmol phenylacetylene, 5 mol% Pd(OAc)$_2$, 0.4 mmol AgBF$_4$, 0.4 mmol triethylamine and 1 mL THF were charged into a 10 mL schlenck tube, the mixture was stirred at 100 °C for 16 hours. 2y was isolated as an oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.93–7.80 (m, 2H), 7.51–7.56 (m, 5H), 7.42–7.46 (m, 1H), 7.34–7.38 (m, 2H), 4.26–4.35 (m, 2H), 1.44 (t, 3H, $J = 11.2$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ 9.74; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.84 (d, $J_{P-C} = 2.9$ Hz), 132.59 (d, $J_{P-C} = 1.6$ Hz), 131.14 (d, $J_{P-C} = 11.2$ Hz), 131.07 (d, $J_{P-C} = 164.6$ Hz), 130.68, 128.60 (d, $J_{P-C} = 14.8$ Hz), 128.56, 119.74 (d, $J_{P-C} = 4.3$ Hz), 101.59 (d, $J_{P-C} = 39.3$ Hz), 81.66 (d, $J_{P-C} = 214.7$ Hz), 62.34 (d, $J_{P-C} = 6.3$ Hz), 16.40 (d, $J_{P-C} = 7.1$ Hz). MS (EI): 270.

Under N$_2$ atmosphere, 0.2 mmol diisoproplyphosphite 1f, 0.4 mmol phenylacetylene, 5 mol% Pd(OAc)$_2$, 0.4 mmol AgBF$_4$, 0.4 mmol Et$_3$N and 1 mL THF were charged into a 10 mL schlenck tube, the mixture was stirred at 100 °C for 16 hours. 2z was isolated as an oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.56 (d, 2H, $J = 6.8$ Hz), 7.45 (t, 1H, $J = 6.8$ Hz), 7.38 (t, 2H, $J = 7.2$ Hz), 4.80–4.84 (m, 2H), 1.42 (d, 12H, $J = 4.2$ Hz); $^{31}$P NMR (162 MHz, CDCl$_3$) δ -8.52; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 132.46 (d, $J_{P-C} = 1.3$ Hz), 130.50, 128.51, 119.74 (d, $J_{P-C} = 5.5$ Hz), 98.11 (d, $J_{P-C} = 52.6$ Hz), 79.74 (d, $J_{P-C} = 297.1$ Hz), 72.33 (d, $J_{P-C} = 5.4$ Hz), 23.89 (d, $J_{P-C} = 4.5$ Hz), 23.61 (d, $J_{P-C} = 4.7$ Hz). MS (EI): 266.


Copies of $^1$H NMR, $^{31}$P NMR and $^{13}$C NMR spectra