

Copper-Catalyzed Synthesis of Alkynylphosphine Derivatives: Unprecedented Use of Nucleophilic Phosphorus compounds

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(I) General remarks

Toluene and THF were purified by an Innovative Technology Pure Solv. Device (activated alumina column containing a copper catalyst and molecular sieves) and degassed. Chromatographic purifications were conducted using Merck silica gel Si 60 (40-63 µm) and TLC were performed on silica gel 60-F₂₅₄ plates (0.1 mm) with UV or KMnO₄ detection. ¹H, ¹³C, ³¹P NMR spectra were recorded on a BRUKER AVANCE III 400 or 500 spectrometer. ¹¹B NMR spectrum was obtained on a 500 spectrometer. ¹H and ¹³C NMR chemical shifts are reported in ppm using the residual peak of chloroform-*d* (7.26 and 77.16 ppm) or tetrahydrofuran-*d*₈ (3.58 and 67.40 ppm) as internal standard. ³¹P and ¹¹B NMR chemical shifts are reported relative to respectively H₃PO₄ (85%) and BF₃.Et₂O used as eternal references. Coupling constants are reported in Hertz (Hz). Abbreviations are used as follows: s = singulet, d = doublet, t = triplet, quint = quintuplet, sext = sextuplet, m = multiplet, br = broad. High Resolution Mass Spectrometry was performed on a Varian MAT 311 spectrometer. IR spectra were recorded on Spectrum One Perkin Elmer spectrometer and only the strongest or structurally most important peaks are listed.

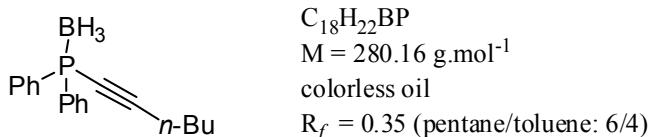
(II) Synthesis of alkynylphosphines **3**

(a) General procedure

In a Schlenk tube, flushed with nitrogen, copper iodide (14.3 mg, 0.075 mmol, 10 mol%), 1,10-phenanthroline (13.5 mg, 0.075 mmol, 10 mol%) and degassed dry toluene (2 mL) were introduced. After 20 min of stirring at rt, phosphine-borane **1** (0.75 mmol, 1 equiv.), K₂CO₃ (207 mg, 1.5 mmol, 2 equiv.) or K₃PO₄ (318 mg, 1.5 mmol, 2 equiv.), degassed dry toluene (7 mL) and a solution of 1-bromoalkyne **2** (0.75 mmol, 1 equiv.) in toluene (3 mL) were successively added. The reaction mixture was flushed with nitrogen prior to thermal heating at 40 °C or 60 °C overnight or until complete conversion of **1** (see Table 2). After cooling to rt, the reaction mixture was filtered over celite with toluene as the eluent. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with pentane/toluene as the eluent.

(b) Characterization data

Hex-1-yndiphenylphosphine borane (3a)



Yield: 74% (155 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.82–7.76 (m, 4 H), 7.50–7.41 (m, 6 H), 2.47 (td, $^4J_{\text{HP}} = 3.2$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 1.63 (quint, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 1.46 (sext, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 0.94 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3 H), 1.70–0.60 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 132.0 (d, $^2J_{\text{CP}} = 11.0$ Hz), 131.5 (d, $^4J_{\text{CP}} = 2.5$ Hz), 129.9 (d, $^1J_{\text{CP}} = 63.7$ Hz), 128.9 (d, $^3J_{\text{CP}} = 10.9$ Hz), 112.9 (d, $^2J_{\text{CP}} = 17.2$ Hz), 70.0 (d, $^1J_{\text{CP}} = 113.9$ Hz), 30.0 (d, $^4J_{\text{CP}} = 1.4$ Hz), 22.1, 20.0 (d, $^3J_{\text{CP}} = 2.4$ Hz), 13.6.

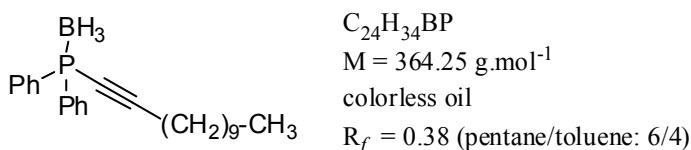
^{31}P NMR (162 MHz, CDCl_3) δ 4.4–4.0 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –35.0 to –40.0 (m).

IR (neat): 2387, 2196, 1437, 1106, 1054, 732, 691 cm^{-1} .

HRMS (ESI) Calcd for $C_{18}H_{22}\text{BNaP} [M+\text{Na}]^+$: 303.1449. Found: 303.1448.

Dodec-1-yndiphenylphosphine borane (3b)



Yield: 69% (189 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.81–7.76 (m, 4 H), 7.50–7.41 (m, 6 H), 2.46 (td, $^4J_{\text{HP}} = 3.2$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 1.64 (quint, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 1.44–1.26 (m, 14 H), 0.88 (t, $^3J_{\text{HH}} = 6.8$ Hz, 3 H), 1.50–0.70 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 132.0 (d, $^2J_{\text{CP}} = 11.1$ Hz), 131.5 (d, $^4J_{\text{CP}} = 2.5$ Hz), 129.9 (d, $^1J_{\text{CP}} = 63.7$ Hz), 128.9 (d, $^3J_{\text{CP}} = 10.9$ Hz), 113.0 (d, $^2J_{\text{CP}} = 17.3$ Hz), 70.1 (d, $^1J_{\text{CP}} = 113.8$ Hz), 32.0, 29.7, 29.6, 29.4, 29.1, 29.0, 28.0, 22.8, 20.3 (d, $^3J_{\text{CP}} = 2.4$ Hz), 14.3.

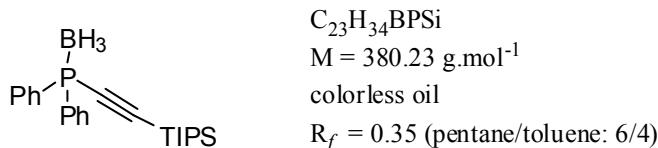
^{31}P NMR (162 MHz, CDCl_3) δ 4.1–3.8 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –35.0 to –39.0 (m).

IR (neat): 2924, 2854, 2390, 2197, 1437, 1107, 1054, 733, 690 cm^{-1} .

HRMS (ESI) Calcd for $C_{24}H_{34}BNaP$ $[M+Na]^+$: 387.2389 Found: 387.2387.

(Triisopropylsilyl)ethynyl diphenylphosphine borane (3c)



Yield: 55% (157 mg, containing 10% of free phosphine).

^1H NMR (400 MHz, CDCl_3) δ 7.84–7.79 (m, 4 H), 7.51–7.42 (m, 6 H), 1.20–1.10 (m, 21 H), 1.70–0.70 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 132.0 (d, $^2J_{CP} = 11.0$ Hz), 131.5 (d, $^4J_{CP} = 2.5$ Hz), 129.5 (d, $^1J_{CP} = 62.9$ Hz), 129.0 (d, $^3J_{CP} = 10.9$ Hz), 117.3 (d, $^2J_{CP} = 7.2$ Hz), 97.3 (d, $^1J_{CP} = 93.4$ Hz), 18.7, 11.2.

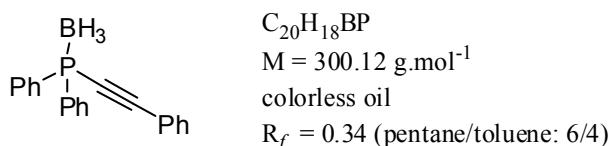
^{31}P NMR (162 MHz, CDCl_3) δ 5.0–4.7 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –35.0 to –39.0 (m).

IR (neat): 2945, 2866, 2393, 2346, 1462, 1437, 1103, 1057, 997, 882, 797, 733, 682 cm^{-1} .

HRMS (ESI) Calcd for $C_{23}H_{34}BNaSiP$ $[M+Na]^+$: 403.2158. Found: 403.2160.

(Phenyl)ethynyl diphenylphosphine borane (3d)



Yield: 69% (148 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.89–7.84 (m, 4 H), 7.61–7.59 (m, 2 H), 7.54–7.36 (m, 9 H), 1.80–0.80 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 132.6 (d, $^4J_{CP} = 1.5$ Hz), 132.1 (d, $^2J_{CP} = 11.1$ Hz), 131.7 (d, $^4J_{CP} = 2.5$ Hz), 130.6, 129.4 (d, $^1J_{CP} = 63.5$ Hz), 129.1 (d, $^3J_{CP} = 11.0$ Hz), 128.7, 120.7 (d, $^3J_{CP} = 3.2$ Hz), 108.8 (d, $^2J_{CP} = 16.8$ Hz), 78.8 (d, $^1J_{CP} = 108.6$ Hz).

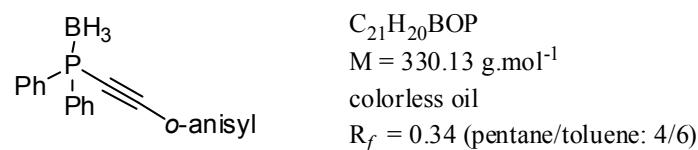
^{31}P NMR (162 MHz, CDCl_3) δ 5.0–4.7 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –34.0 to –39.0 (m).

IR (neat): 2388, 2177, 1489, 1437, 1105, 1053, 854, 732, 686 cm^{-1} .

HRMS (ESI) Calcd for $C_{20}H_{18}BNaP$ $[M+Na]^+$: 323.1137. Found: 323.1133.

(*o*-anisyl)ethynyl diphenylphosphine borane (3e**)**



Yield: 59% (146 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.96–7.90 (m, 4 H), 7.54–7.38 (m, 8 H), 6.97–6.91 (m, 2 H), 3.92 (s, 3 H), 1.77–0.77 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 161.6 (d, $^4J_{\text{CP}} = 1.1$ Hz), 134.1 (d, $^4J_{\text{CP}} = 1.6$ Hz), 132.2 (d, $^2J_{\text{CP}} = 11.2$ Hz), 132.1, 131.5 (d, $^4J_{\text{CP}} = 2.5$ Hz), 129.9 (d, $^1J_{\text{CP}} = 63.4$ Hz), 128.9 (d, $^3J_{\text{CP}} = 10.9$ Hz), 120.6, 111.0, 110.2 (d, $^3J_{\text{CP}} = 3.2$ Hz), 106.0 (d, $^2J_{\text{CP}} = 17.6$ Hz), 82.4 (d, $^1J_{\text{CP}} = 111.4$ Hz), 56.0.

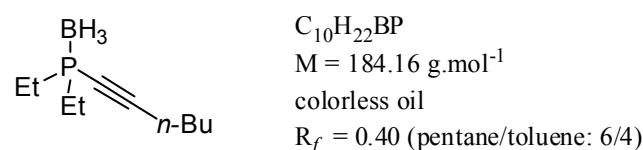
^{31}P NMR (162 MHz, CDCl_3) δ 4.8–4.6 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –36.0 to –41.0 (m).

IR (neat): 2376, 2176, 1489, 1436, 1258, 1106, 1053, 1021, 867, 732, 690 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{20}\text{OBNaP} [\text{M}+\text{Na}]^+$: 353.1242. Found: 353.1245.

Diethylhex-1-ynylphosphine borane (3f**)**



Yield: 60% (106 mg), obtained from **1b** (100 mg, 0.96 mmol).

^1H NMR (400 MHz, CDCl_3) δ 2.34 (td, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HP}} = 3.3$ Hz, 2 H), 1.82–1.65 (m, 4 H), 1.55 (quint, $^3J_{\text{HH}} = 6.8$ Hz, 2 H), 1.41 (sext, $^3J_{\text{HH}} = 7.0$ Hz, 2 H), 1.20 (dt, $^3J_{\text{HP}} = 17.6$ Hz, $^3J_{\text{HH}} = 7.6$ Hz, 6 H), 0.92 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H), 0.96–0.12 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 110.1 (d, $^2J_{\text{CP}} = 12.6$ Hz), 69.9 (d, $^1J_{\text{CP}} = 95.5$ Hz), 30.1 (d, $^4J_{\text{CP}} = 1.5$ Hz), 22.0, 19.7 (d, $^3J_{\text{CP}} = 2.3$ Hz), 19.0 (d, $^1J_{\text{CP}} = 41.0$ Hz), 13.6, 7.4 (d, $^2J_{\text{CP}} = 3.5$ Hz).

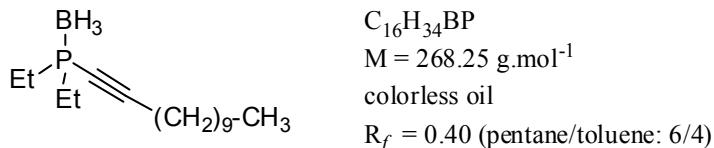
^{31}P NMR (162 MHz, CDCl_3) δ 8.8 (q, $^1J_{\text{PB}} = 58.9$ Hz).

^{11}B NMR (160 MHz, CDCl_3) δ –39.2 (dq, $^1J_{\text{BH}} = 96.0$ Hz, $^1J_{\text{BP}} = 58.9$ Hz).

IR (neat): 2961, 2937, 2390, 2197, 1457, 1067, 1045, 1034, 1020, 777, 760 cm^{-1} .

HRMS (ESI) Calcd for $\text{C}_{10}\text{H}_{22}\text{BNaP} [\text{M}+\text{Na}]^+$: 207.1450. Found: 207.1459.

Dodec-1-ynyldiethylphosphine borane (**3g**)



Yield: 58% (149 mg), obtained from **1b** (100 mg, 0.96 mmol).

^1H NMR (400 MHz, CDCl_3) δ 2.32 (td, $^4J_{\text{HP}} = 3.2$ Hz, $^3J_{\text{HH}} = 6.8$ Hz, 2 H), 1.82–1.64 (m, 4 H), 1.54 (quint, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 1.41–1.24 (m, 14 H), 1.19 (dt, $^3J_{\text{HP}} = 17.5$ Hz, $^3J_{\text{HH}} = 7.6$ Hz, 6 H), 0.87 (t, $^3J_{\text{HH}} = 7.2$ Hz, 3 H), 0.90–0.10 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 110.1 (d, $^2J_{\text{CP}} = 12.7$ Hz), 69.9 (d, $^1J_{\text{CP}} = 95.4$ Hz), 32.0, 29.6, 29.5, 29.4, 29.1, 28.8, 28.0 (d, $^4J_{\text{CP}} = 1.4$ Hz), 22.8, 19.9 (d, $^3J_{\text{CP}} = 2.3$ Hz), 19.0 (d, $^1J_{\text{CP}} = 41$ Hz), 14.2, 7.3 (d, $^2J_{\text{CP}} = 3.5$ Hz).

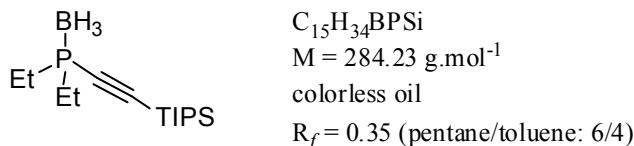
^{31}P NMR (162 MHz, CDCl_3) δ 9.3–8.2 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –39.2 (dq, $^1J_{\text{BH}} = 96.5$ Hz, $^1J_{\text{BP}} = 58.7$ Hz).

IR (neat): 2924, 2854, 2379, 2196, 1457, 1066, 1045, 1019, 777, 760 cm^{-1} .

HRMS (ESI) Calcd for $C_{16}H_{34}BNaP$ [$M+\text{Na}^+$]: 291.2389. Found: 291.2390.

Diethyl(triisopropylsilyl)ethynylphosphine borane (**3h**)



Yield: 58% (158 mg), obtained from **1b** (100 mg, 0.96 mmol).

^1H NMR (400 MHz, CDCl_3) δ 1.79–1.68 (m, 4 H), 1.24 (dt, $^3J_{\text{HP}} = 17.2$ Hz, $^3J_{\text{HH}} = 7.6$ Hz, 6 H), 1.11–1.07 (m, 21 H), 0.95–0.24 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 114.0 (d, $^2J_{\text{CP}} = 3.6$ Hz), 97.8 (d, $^1J_{\text{CP}} = 76.6$ Hz), 19.0 (d, $^1J_{\text{CP}} = 40.1$ Hz), 18.6, 11.1, 7.4 (d, $^2J_{\text{CP}} = 3.7$ Hz).

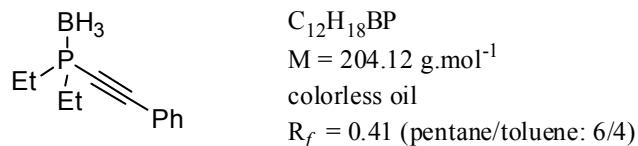
^{31}P NMR (162 MHz, CDCl_3) δ 10.1–9.7 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –39.2 (dq, $^1J_{\text{BH}} = 95.8$ Hz, $^1J_{\text{BP}} = 55.8$ Hz).

IR (neat): 2943, 2867, 2379, 2346, 1461, 1065, 1036, 1019, 997, 882, 805 cm^{-1} .

HRMS (ESI) Calcd for $C_{15}H_{34}BNaSiP$ [$M+\text{Na}^+$]: 307.2158. Found: 307.2157.

Diethyl(phenyl)ethynylphosphine borane (**3i**)



Yield: 59% (115 mg), obtained from **1b** (100 mg, 0.96 mmol).

^1H NMR (400 MHz, CDCl_3) δ 7.53–7.51 (m, 2 H), 7.42–7.33 (m, 3 H), 1.96–1.77 (m, 4 H), 1.29 (dt, $^3J_{\text{HP}} = 17.5$ Hz, $^3J_{\text{HH}} = 7.6$ Hz, 6 H), 1.10–0.20 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 132.5 (d, $^4J_{\text{CP}} = 1.6$ Hz), 130.2, 128.6, 120.9 (d, $^3J_{\text{CP}} = 3.1$ Hz), 106.6 (d, $^2J_{\text{CP}} = 12.0$ Hz), 79.0 (d, $^1J_{\text{CP}} = 89.9$ Hz), 19.0 (d, $^1J_{\text{CP}} = 40.4$ Hz), 7.5 (d, $^2J_{\text{CP}} = 3.5$ Hz).

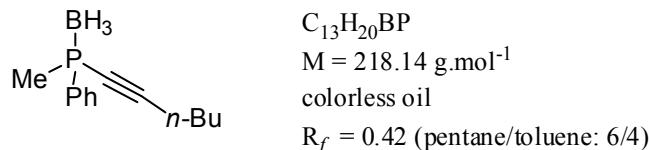
^{31}P NMR (162 MHz, CDCl_3) δ 10.4–10.0 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –39.2 (dq, $^1J_{\text{BH}} = 96.7$ Hz, $^1J_{\text{PB}} = 56.2$ Hz).

IR (neat): 2379, 2336, 2178, 1489, 1065, 1034, 1020, 850, 755, 688 cm^{-1} .

HRMS (ESI) Calcd for $C_{12}H_{18}BNaP$ [$M+Na$] $^+$: 227.1137. Found: 227.1137.

Hex-1-ynylmethylphenylphosphine borane (**3j**)



Yield: 50% (82 mg).

^1H NMR (400 MHz, CDCl_3) δ 7.86–7.81 (m, 2 H), 7.52–7.45 (m, 3 H), 2.39 (td, $^4J_{\text{HP}} = 3.2$ Hz, $^3J_{\text{HH}} = 7.1$ Hz, 2 H), 1.70 (d, $^2J_{\text{HP}} = 10.5$ Hz, 3 H), 1.59 (quint, $^3J_{\text{HH}} = 7.0$ Hz, 2 H), 1.43 (sext, $^3J_{\text{HH}} = 7.2$ Hz, 2 H), 0.93 (t, $^3J_{\text{HH}} = 7.3$ Hz, 3 H), 1.40–0.50 (m, 3 H).

^{13}C NMR (100 MHz, CDCl_3) δ 131.6 (d, $^4J_{\text{CP}} = 2.5$ Hz), 131.3 (d, $^2J_{\text{CP}} = 10.8$ Hz), 129.9 (d, $^1J_{\text{CP}} = 62.8$ Hz), 128.9 (d, $^3J_{\text{CP}} = 10.8$ Hz), 110.9 (d, $^2J_{\text{CP}} = 16.4$ Hz), 71.1 (d, $^1J_{\text{CP}} = 106.9$ Hz), 29.9 (d, $^4J_{\text{CP}} = 1.5$ Hz), 22.1, 19.8 (d, $^3J_{\text{CP}} = 2.4$ Hz), 16.1 (d, $^1J_{\text{CP}} = 44$ Hz), 13.6.

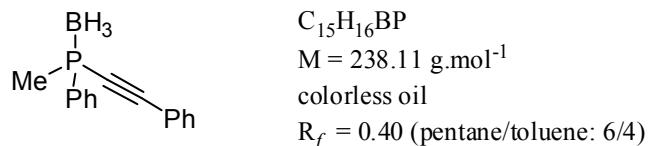
^{31}P NMR (162 MHz, CDCl_3) δ –4.4 to –4.9 (m).

^{11}B NMR (160 MHz, CDCl_3) δ –36.8 (dq, $^1J_{\text{BH}} = 96.7$ Hz, $^1J_{\text{PB}} = 54.7$ Hz).

IR (neat): 2379, 2354, 2197, 1438, 1110, 1058, 909, 894, 742, 691 cm^{-1} .

HRMS (ESI) Calcd for $C_{13}H_{20}BNaP$ [$M+Na$] $^+$: 241.1293. Found: 241.1293.

(Phenyl)ethynylmethylphenylphosphine borane (3k)



Yield: 52% (93 mg).

¹H NMR (400 MHz, CDCl₃) δ 7.96–7.90 (m, 2 H), 7.57–7.34 (m, 8 H), 1.83 (d, ²J_{HP} = 10.4 Hz, 3 H), 1.50–0.60 (m, 3 H).

¹³C NMR (100 MHz, CDCl₃) δ 132.4 (d, ⁴J_{CP} = 1.7 Hz), 131.8 (d, ⁴J_{CP} = 2.6 Hz), 131.4 (d, ²J_{CP} = 10.9 Hz), 130.4, 129.2 (d, ¹J_{CP} = 62.5 Hz), 129.0 (d, ³J_{CP} = 10.8 Hz), 128.6, 120.6 (d, ³J_{CP} = 3.2 Hz), 107.0 (d, ²J_{CP} = 15.9 Hz), 79.9 (d, ¹J_{CP} = 101.4 Hz), 15.7 (d, ¹J_{CP} = 43.8 Hz).

³¹P NMR (162 MHz, CDCl₃) δ –3.5 to –3.9 (m).

¹¹B NMR (160 MHz, CDCl₃) δ –36.8 (dq, ¹J_{BH} = 95.9 Hz, ¹J_{PB} = 52.0 Hz).

IR (neat): 2373, 2178, 1488, 1437, 1110, 1057, 895, 741, 687 cm⁻¹.

HRMS (ESI) Calcd for C₁₅H₁₆BNaP [M+Na]⁺: 261.0980. Found: 261.0987.

(III) Formation of complex [Ph₂P(BH₃)Cuphen] and Reaction with 1-bromohexyne **2a**

In a Schlenk tube, flushed with nitrogen, diphenylphosphine-borane **1a** (60 mg, 0.30 mmol, 1 equiv.) in degassed dry THF (0.5 mL) was cooled to –78 °C. *n*-BuLi (0.130 mL, 0.33 mmol, 1.1 equiv., 2.5 M solution in hexane) was then slowly added and the mixture was stirred at this temperature for 20 min before allowing the temperature to reach 0 °C. The resulting solution of Ph₂P(BH₃)Li (δ_p = –31.0 ppm) was slowly added to a suspension of CuI (57 mg, 0.30 mmol, 1 equiv.) in degassed dry toluene (1 mL) at 0 °C. After 20 min of stirring at 0 °C, a solution of 1,10-phenanthroline (54 mg, 0.30 mmol, 1 equiv.) in a mixture of degassed dry toluene (0.5 mL) and THF (0.3 mL) was added. The reaction medium turned red instantly, indicating the formation of [Ph₂P(BH₃)Cuphen] complex (δ_p = –22.0 ppm). After 20 min at 0 °C, a pre-cooled solution of 1-bromohexyne **2a** (70 mg, 0.43 mmol, 1.4 equiv.) in degassed dry toluene (0.5 mL) was slowly added and the reaction mixture was subsequently heated to 40 °C. After 2 hours, the spectrum showed the signal of the corresponding alkynylphosphine **3a** (δ_p = 5.0 ppm), alongside with a broad signal (δ_p = –33.1 to –35.7 ppm)

assigned to [Ph₂PHCuXphen] complexes (X = I, Br) and a signal corresponding to **1a** (δ_p = 1.4 ppm), probably resulting from a partial hydrolysis of the copper phosphide [Ph₂P(BH₃)Cuphen].

NMR data for [Ph₂P(BH₃)Cuphen]:

¹H NMR (500 MHz, THF-d₈) δ 8.80 (br, 2 H), 8.26 (br, 2 H), 7.64–7.57 (m, 8 H), 6.97 (br, 6 H), (signal of BH₃ is hidden in the base line).

¹³C NMR (125 MHz, THF-d₈) δ 150.3, 144.3 (d br, $^1J_{CP}$ = 16.3 Hz), 144.0, 137.2 (br), 134.6 (br), 129.6, 127.6 (d br, $^3J_{CP}$ = 5.5 Hz), 127.3, 126.7, 125.3.

³¹P NMR (202 MHz, THF-d₈) δ –21.8 (br).

¹¹B NMR (160 MHz, THF-d₈) δ –31.0 (br).

(IV) NMR Spectra

