Supplementary Information

Double Hydrophosphinination of Alkynes Promoted by Rhodium: the Key Role of an N-Heterocyclic Carbene Ligand

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Experimental Section

All reactions were carried out under argon atmosphere with rigorous exclusion of air. Alkynes were purchased from commercial sources and were used as received. Organic solvents were dried by standard procedures and distilled under argon prior to use or obtained oxygen- and water-free from a Solvent Purification System (Innovative Technologies). The organometallic catalysts \([\text{Rh}(\mu-\text{Cl})(\text{IPr})(\eta^2\text{-coe})]_2 (1a)\),\[1\] \([\text{Rh}(\mu-\text{Cl})(\eta^2\text{-coe})]_2 (1b)\),\[2\] \(\text{RhCl}(\text{PPh}_3)_3 (1c)\),\[3\] \([\text{Rh}(\mu-\text{Cl})(\text{PCy}_3)(\eta^2\text{-coe})]_2 (1d)\),\[4\] were prepared following the procedures described in the literature. The diphosphines \(7a, b, e\) were previously reported and fully characterized.\[5-8\] \(^1\text{H}, \ ^{31}\text{P}\{^1\text{H}\}, \ ^{19}\text{F}\{^1\text{H}\}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra were recorded on either a Varian Gemini 2000, a Bruker ARX 300 or a Bruker Avance 500 and 400 MHz instrument. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks \(\left( ^1\text{H}, \ ^{13}\text{C}\{^1\text{H}\}\right)\) or external \(\text{H}_3\text{PO}_4\) \(\left( ^{31}\text{P}\right)\), and \(\text{CFCl}_3\) \(\left( ^{19}\text{F}\right)\). Coupling constants, \(J\), are given in Hz. Spectral assignments were achieved by combination of \(^1\text{H}\{^{31}\text{P}\}\), \(^1\text{H}-^1\text{H}\) COSY, \(^{13}\text{C}\{^1\text{H}\}-\text{APT}, \ ^1\text{H}-^{13}\text{C}\) HSQC/HMBC, and \(^1\text{H}-^{31}\text{P}\) HMBC experiments. High-resolution electrospray mass spectra were acquired on a Bruker Microtof-Q (ESI\(^+\)).
Table S1. Reaction of phenylacetylene with diphenylphosphine catalyzed by Rh\textsuperscript{i} complexes.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>T (°C)</th>
<th>Alkyne/Ph\textsubscript{2}PH molar ratio</th>
<th>Catalyst\textsuperscript{b}</th>
<th>Solvent</th>
<th>Conv. (%)\textsuperscript{c}</th>
<th>4a/5a/6a (%)\textsuperscript{d}</th>
<th>7a (%)\textsuperscript{a}</th>
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\textsuperscript{a} Reaction conditions: 0.2 mmol of phenylacetylene, 0.2 mmol of Ph\textsubscript{2}PH, 0.5 mL of solvent, 24 h of reaction. \textsuperscript{b} Rh/PhPH\textsubscript{2}=0.05. \textsuperscript{c} Based on phosphine consumption, quantified by integration of the Inverse Gated Decoupled-\textsuperscript{31}P NMR spectra. \textsuperscript{d} Molar ratio, quantified by integration of the Inverse Gated Decoupled-\textsuperscript{31}P NMR spectra. \textsuperscript{e} Rh/PhPH\textsubscript{2}=0.025. \textsuperscript{f} 0.2 mmol of phenylacetylene, 1 mmol of Ph\textsubscript{2}PH. \textsuperscript{g} Based on phenylacetylene consumption, quantified by integration of the \textsuperscript{1}H-NMR spectra. \textsuperscript{h} 1 mmol of phenylacetylene, 0.2 mmol of Ph\textsubscript{2}PH. \textsuperscript{i} 0.2 mmol of Ph\textsubscript{2}PH. \textsuperscript{j} 0.1 mmol of phenylacetylene, 0.2 mmol of Ph\textsubscript{2}PH. \textsuperscript{k} 0.4 mmol of phenylacetylene, 0.8 mmol of Ph\textsubscript{2}PH and 0.02 mmol of 1a. \textsuperscript{1} 0.2 mmol of Ph\textsubscript{2}PH.
In-situ preparation of RhCl(iPr)(PHPh₂)₂ (9).

A solution of 1a (25 mg, 0.020 mmol) in C₆D₆ (0.5 mL, NMR-tube) at room temperature was treated with diphenylphosphine (16 μL, 0.092 mmol). It was immediately observed the formation of 9. ¹H NMR (300 MHz, toluene-d₈, 298 K): δ 7.58 – 6.79 (H Ph, 26H), 6.83 (s, 2H, =CHN), 6.39 (d, Jₚ-H = 330, 1H, PₐH), 5.46 (d, Jₚ-H = 331, 1H, PₐH), 4.10 (sept, Jₖ-H = 7, 2H, CHMeᵢPr), 3.24 (sept, Jₖ-H = 7, 1H, CHMeᵢPr), 0.99 (d, Jₖ-H = 7, 1H, CHMeᵢPr), 1.49 (d, Jₖ-H = 7, 1H, CHMeᵢPr), 0.90 (d, Jₖ-H = 7, 1H, CHMeᵢPr).

Preparation of RhCl(iPr)(rac-Phenphos) (10a,b).

A yellow solution of 1a (100 mg, 0.078 mmol) in toluene (10 mL) was treated with 7a (74 mg, 0.157 mmol) and stirred at room temperature for 1 h. The solution was concentrated to ca. 1 mL and then n-hexane (3 mL) was added to induce the precipitation of a yellow solid which was washed with hexane (3 x 3 mL) and dried in vacuo. The compound was obtained as a diastereomer mixture of 10a/10b in a 98/2 ratio. Yield: 141 mg (90%). 10a: ¹H NMR (500 MHz, C₆D₆, 298 K): δ 7.81 – 6.76 (H Ph, 31H), 4.93 (sept, Jₖ-H = 7, 1H, CHMeᵢPr), 3.85 (sept, Jₖ-H = 7, 1H, CHMeᵢPr), 3.32 (sept, Jₖ-H = 7, 1H, CHMeᵢPr), 2.74 (sept, Jₖ-H = 7,
1H, CHMeIPr), 3.32 (overlapped, 1H, CHP), 2.61 – 2.50 (m, 1H, CH2P), 2.43-
2.30 (m, 1H, CH2P), 1.87 (d, JH-H = 7, 3H, CHMeIPr), 1.37 (d, JH-H = 7, 3H,
CHMeIPr), 1.28 (d, JH-H = 7, 3H, CHMeIPr), 1.20 (d, JH-H = 7, 3H, CHMeIPr), 1.09
(d, JH-H = 7, 3H, CHMeIPr), 1.06 (d, JH-H = 7, 3H, CHMeIPr), 0.97 (d, JH-H = 7, 3H,
CHMeIPr), 0.36 (d, JH-H = 7, 3H, CHMeIPr). 13C{1H}-APT NMR (125 MHz, C6D6,
298 K): δ 195.9 (ddd, JC-P = 121, JC-Rh = 47, JC-P = 12, Rh-CIPr), 149.4 (s, Cq-IPr),
149.2 (s, Cq-IPr), 144.9 (s, Cq-IPr), 143.7 (s, Cq-IPr), 138.1 (s, CqN), 137.5 (s, CqN),
149.0 – 122.1 (CPh), 42.2 (dd, JC-P = 19, 15, CHP), 39.5 (dd, JC-P = 36, 29, CH2-
P), 29.4 (s, CHMeIPr), 28.7 (s, CHMeIPr), 28.6 (s, CHMeIPr), 28.2 (s, CHMeIPr),
27.5 (s, CHMeIPr), 26.7 (s, CHMeIPr), 26.1 (s, CHMeIPr), 25.6 (s, CHMeIPr), 24.4
(s, CHMeIPr), 24.2 (s, CHMeIPr), 23.8 (s, CHMeIPr), 22.6 (s, CHMeIPr). 31P{1H}
NMR (202 MHz, C6D6, 298 K): δ 78.1 (dd, JRh-P = 122, JP-P = 44, P-CH), 45.9
(dd, JRh-P = 203, JP-P = 44, P-CH2).

10b: 31P{1H} NMR (202 MHz, C6D6, 298 K): δ 74.2 (dd, JRh-P = 210, JP-P = 44, P-
CH), 46.6 (dd, JRh-P = 122, JP-P = 44, P-CH2).

**Reaction of 10 with PHPh2.**

A solution of 10 (10 mg, 0.01 mmol) in C6D6 (0.5 mL, NMR-tube) at room
temperature was treated with PHPh2 (3.5 μL, 0.02 mmol). The solution was
heated at 333 K (60°C) in a NMR spectrometer and the interconversion
between 10a,b and 9 quantified every 10 min by integration of the Inverse
Gated Decoupled-31P NMR spectra. After 5 h 10b was totally undetectable and
a 10a:9 molar ratio of 79:21 was measured. This value remained unchanged in
the next 5 h where upon the formation of tetraphenylbiphosphine (8) decreases
the amount of both complexes.
Preparation of [RhCl(dppe)₂]Cl (11).

Complex 11 was prepared according to a modified literature method and its spectra were consistent with that of the published data.⁹ A red solution of [RhCl(PPh₃)₃] (1c) (104 mg, 0.112 mmol) in CH₂Cl (10 mL) at room temperature was treated with {1,2-bis(diphenylphosphino)ethane} (dppe) (90 mg, 0.224 mmol) and stirred at room temperature for 1 h. The solution was concentrated to ca. 1 mL and then diethylether (3 mL) was added to induce the precipitation of a yellow solid which was washed with diethylether (3 x 3 mL) and dried in vacuo. Yield: 96 mg (92%).

Standard procedure for the catalytic hydrophosphination of alkynes. In a Young type NMR tube 0.005 mol of catalyst 1a were dissolved in 0.4 mL of toluene + 0.1 mL of C₆D₆ and then 0.2 mmol of phosphine and 0.1 mmol of alkyne were added and the solution was heated at 120 °C. Conversion was quantified by integration of ³¹P{¹H} NMR spectra. Inverse Gated Decoupling was employed to obtain ¹H decoupled NMR spectra of ³¹P nuclei without signal enhancement by nuclear Overhauser effects (NOE). To observe all components in the sample, a full spectrum was recorded with 256 scans using a 200 ppm spectral width, 101K data points, 0.99-s acquisition time, a relaxation delay of 5 s, and a 30° pulse width. A typical example of ³¹P{¹H} NMR spectra corresponding to the hydrophosphination of phenylacetylene (entry 3, Table S1) is shown below (peak marked with X correspond to PPh₃, an impurity already present in the commercial Ph₂PH).
Reaction of phenylacetylene and diphenylphosphine.

Preparation of (1-phenylethane-1,2-diyl)bis(diphenylphosphine) (rac-Phenphos) (7a).

In a schlenk tube 64 mg of 1a (0.05 mmol) in 10 mL of toluene was treated with 110 μL of phenylacetylene (1 mmol), 350 μL of Ph₂PH (2 mmol) and magnetically stirred for 24 h at 120 °C. At the end of the reaction, the volatiles were removed in vacuo. The residue was dissolved in 10 mL of dichloromethane and filtered through a short column (5 cm) of silica. The resulted solution was concentrated to ca. 1 mL and then methanol (10 mL) was added to induce the precipitation of a fluffy off-white solid which was washed with methanol (3 x 10 mL) cold hexane (3 x 2 mL) and dried in vacuo. Yield: 195 mg (41%). The NMR spectrum was consistent with that of the published data.⁵

¹H NMR (300 MHz, C₆D₆, 298 K): δ 7.67 – 6.91 (25H, CH Ph), 3.77 – 3.66 (m, 1H, CHP), 2.89 – 2.77 (m, 2H, CH₂P). ¹³C{¹H}-APT NMR (75 MHz, C₆D₆, 298
K): $\delta$ 141.0 – 126.3 (C<sub>Ph</sub>), 42.3 (dd, $J_{C-P} = 16$, 15, CHP), 32.9 (dd, $J_{C-P} = 22$, 17, CH<sub>2</sub>P). $^{31}$P({<sup>1</sup>H}) NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): $\delta$ 2.8 (d, $J_{P-P} = 18$, CHP), -21.2 (d, $J_{P-P} = 18$, CH<sub>2</sub>P).

diphenyl(1-phenylvinyl)phosphine (4a)

The NMR spectrum was consistent with that of the published data.<sup>10</sup> $^1$H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): $\delta$ 7.49 – 7.24 (15H, CH<sub>Ph</sub>), 6.00 (dd, 1H, $J_{H-P}$ = 13, $J_{H-H}$ = 1, =$CH_{(trans-P)}$), 5.15 (dd, 1H, $J_{H-P}$ = 6, $J_{H-H}$ = 1, =$CH_{(cis-P)}$). $^{31}$P({<sup>1</sup>H}) NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): $\delta$ -4.7 (s).

(Z)-diphenyl(styryl)phosphine (5a)

The NMR spectrum was consistent with that of the published data.<sup>10</sup> $^1$H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): $\delta$ 7.52 – 7.30 (15H, CH<sub>Ph</sub>), 7.28 (overlapped, 1H, =$CHP$), 6.50 (dd, 1H, $J_{H-H}$ = 13, $J_{H-P}$ = 3, =$CHPh$). $^{31}$P({<sup>1</sup>H}) NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): $\delta$ -24.1 (s).

(E)-diphenyl(styryl)phosphine (6a)

The NMR spectrum was consistent with that of the published data.<sup>10</sup> $^1$H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): $\delta$ 7.61 – 7.28 (15H, CH<sub>Ph</sub>), 7.49 (overlapped, 1H, =$CHP$), 6.95 (overlapped, 1H, =$CHPh$). $^{31}$P({<sup>1</sup>H}) NMR (121 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): $\delta$ -11.3 (s).
tetraphenylbiphosphine (8)

The NMR spectrum was consistent with that of the published data.[11] $^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): $\delta$ 7.42 – 7.01 (20H, CH$_2$Ph). $^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$, 298 K): -14.7 (s).

**NMR spectra of 7a**

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K)
$^{31}\text{P}[^1\text{H}]$ NMR (121 MHz, C$_6$D$_6$, 298 K)

$^{13}\text{C}[^1\text{H}]$-APT NMR (75 MHz, C$_6$D$_6$, 298 K)
Reaction of 4-methoxyphenylacetylene and diphenylphosphine.

(1-(4-methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine) (7b)

\[
\begin{align*}
\text{1H NMR (300 MHz, C}_6\text{D}_6, 298 K):} & \quad \delta 7.68 - 6.63 (24H, CH}_2\text{Ph), 3.74 - 3.67 (m, 1H, CHP), 3.27 (s, 3H, OMe), 2.86 - 2.84 (m, 2H, CH}_2\text{P), 2.83 - 2.75 (m, 2H, CH}_2\text{P).} \\
\text{13C}^1\text{H}-\text{APT NMR (75 MHz, C}_6\text{D}_6, 298 K):} & \quad \delta 158.6 (d, J_{C-P} = 2, C_\text{qOCH}_3), 140.1 - 113.7 (C \text{Ph}), 54.5 (s, OCH}_3), 41.5 (dd, J_{C-P} = 16, 15, CHP), 33.9 (dd, J_{C-P} = 23, 17, CH}_2\text{P).} \\
\text{31P}^1\text{H} \text{NMR (121 MHz, C}_6\text{D}_6, 298 K):} & \quad \delta 1.8 (d, J_{P-P} = 17, CHP), -21.2 (d, J_{P-P} = 17, CH}_2\text{P).}
\end{align*}
\]

(Z)-(4-methoxystyryl)diphenylphosphine (5b)

\[
\begin{align*}
\text{1H NMR (300 MHz, C}_6\text{D}_6, 298 K):} & \quad \delta 7.48 - 7.25 (14H, CH}_2\text{Ph), 7.30 (overlapped, 1H, =CHP), 6.43 (dd, 1H, J_{H-H} = 13, J_{H-P} = 3, =CHPh), 3.41 (s, 3H, OMe).} \\
\text{31P}^1\text{H} \text{NMR (121 MHz, C}_6\text{D}_6, 298 K):} & \quad \delta -23.6 (s).
\end{align*}
\]

(E)-(4-methoxystyryl)diphenylphosphine (6b)

\[
\begin{align*}
\text{1H NMR (300 MHz, C}_6\text{D}_6, 298 K):} & \quad \delta 7.69 - 7.20 (14H, CH}_2\text{Ph), 7.23 (overlapped, 1H, =CHP), 6.97 (dd, 1H, J_{H-H} = 17, J_{H-P} = 6, =CHPh), 3.32 (s, 3H, OMe).} \\
\text{31P}^1\text{H} \text{NMR (121 MHz, C}_6\text{D}_6, 298 K):} & \quad \delta -11.2 (s).
\end{align*}
\]
NMR spectra of the reaction crude.

Reaction conditions: 4-methoxyphenylacetylene (0.2 mmol), Ph₂PH (0.2 mmol), 1a (0.005 mmol), C₆D₆ (0.5 mL), 48 h at 80 °C.

¹H NMR (300 MHz, C₆D₆, 298 K)
$^{31}$P($^1$H) NMR (121 MHz, C$_6$D$_6$, 298 K)

$^{13}$C($^1$H)-APT NMR (75 MHz, C$_6$D$_6$, 298 K)
Reaction of 4-trifluoromethylphenylacetylene and diphenylphosphine.

(1-(4-(trifluoromethyl)phenyl)ethane-1,2-diyl)bis(diphenylphosphine) (7c)

\[ \text{1H NMR (300 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 7.63 - 6.81 (24H, CH}_\text{Ph}), 3.74 - 3.68 (m, 1H, CHP), 2.8 - 2.78 (m, 2H, CH}_2\text{P), 2.76 - 2.69 (m, 2H, CH}_2\text{P).} \]

\[ \text{13C}^{1\text{H}}\text{-APT NMR (75 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 142.4 - 114.9 (C}_\text{Ph}, 42.5 (dd, J_C-P = 17, 16, CHP), 32.9 (dd, J_C-P = 21, 18, CH}_2\text{P).} \]

\[ \text{31P}^{1\text{H}}\text{ NMR (121 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 4.2 (d, J_P-P = 17, CHP), -20.1 (d, J_P-P = 17, CH}_2\text{P).} \]

\[ \text{19F NMR (228 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -62.1 (s, CF}_3\text{).} \]

(Z)-diphenyl(4-(trifluoromethyl)styryl)phosphine (5c)

\[ \text{1H NMR (300 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 7.54 - 7.07 (14H, CH}_\text{Ph}), 7.10 (overlapped, 1H, =CHP), 6.57 (dd, 1H, J_H-H = 13, J_H-P = 2, =CHPh). \]

\[ \text{31P}^{1\text{H}}\text{ NMR (121 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -24.1 (s). \]

\[ \text{19F NMR (228 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -62.0 (s, CF}_3\text{).} \]

(E)-diphenyl(4-(trifluoromethyl)styryl)phosphine (6c)

\[ \text{1H NMR (300 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 7.62 - 7.24 (14H, CH}_\text{Ph}), 7.03 (overlapped, 1H, =CHP), 6.85 (dd, 1H, J_H-H = 17, J_H-P = 11, =CHPh). \]

\[ \text{31P}^{1\text{H}}\text{ NMR (121 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -10.8 (s). \]

\[ \text{19F NMR (228 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -61.7 (s, CF}_3\text{).} \]
NMR spectra of the reaction crude.

Reaction conditions: 4-trifluoromethylphenylacetylene (0.2 mmol), Ph$_2$PH (0.2 mmol), 1a (0.005 mmol), C$_6$D$_6$ (0.5 mL), 48 h at 80 °C.

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K)
$^{31}$P$^{[1H]}$ NMR (121 MHz, $C_6D_6$, 298 K)

$^{13}$C$^{[1H]}$-APT NMR (75 MHz, $C_6D_6$, 298 K)
Reaction of 3-methoxyphenylacetylene and diphenylphosphine.

(1-(3-methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine) (7d)

![Chemical structure](image)

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 7.71 – 6.68 (24H, CH$_2$Ph), 3.77 – 3.65 (m, 1H, CHP), 3.38 (s, 3H, OMe), 2.88 – 2.81 (m, 2H, CH$_2$P). $^{13}$C($^1$H)-APT NMR (75 MHz, C$_6$D$_6$, 298 K): δ 159.9 (s, C$_q$OCH$_3$), 140.8 – 133.5 (C$_{Ph}$), 54.4 (s, OCH$_3$), 42.5 (dd, $J_{C-P} = 16$, 15, CHP), 33.5 (dd, $J_{C-P} = 22$, 17, CH$_2$P). $^{31}$P($^1$H) NMR (121 MHz, C$_6$D$_6$, 298 K): δ 2.5 (d, $J_{P-P} = 18$, CHP), -20.9 (d, $J_{P-P} = 18$, CH$_2$P).

(Z)-(3-methoxystyryl)diphenylphosphine (5d)

![Chemical structure](image)

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 7.60 – 7.13 (14H, CH$_2$Ph), 7.29 (overlapped, 1H, =CHP), 6.52 (dd, 1H, $J_{H-H} = 13$, $J_{H-P} = 2$, =CHPh), 3.40 (s, 3H, OMe). $^{31}$P($^1$H) NMR (121 MHz, C$_6$D$_6$, 298 K): δ -23.2 (s).

(E)-(3-methoxystyryl)diphenylphosphine (6d)

![Chemical structure](image)

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 7.65 – 7.22 (14H, CH$_2$Ph), 7.13 (overlapped, 1H, =CHP), 6.83 (overlapped, 1H, =CHPh), 3.43 (s, 3H, OMe). $^{31}$P($^1$H) NMR (121 MHz, C$_6$D$_6$, 298 K): δ -11.3 (s).
NMR spectra of the reaction crude.

Reaction conditions: 1-ethynyl-3-methoxybenzene (0.2 mmol), Ph$_2$PH (0.2 mmol), 1a (0.005 mmol), C$_6$D$_6$ (0.5 mL), 72 h at 80 °C.

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K)
$^{31}\text{P}^{\text{1H}}$ NMR (121 MHz, C$_6$D$_6$, 298 K)

$^{13}\text{C}^{\text{1H}}$-APT NMR (75 MHz, C$_6$D$_6$, 298 K)
Reaction of 2-ethynylpyridine and diphenylphosphine.

2-(1,2-bis(diphenylphosphanyl)ethyl)pyridine (7e)

\[
\begin{align*}
\delta & 8.48 - 8.44 (m, 1H, H_{2-py}), 7.58 - 6.77 (23H, CH_{Ph}), 3.93 - 3.83 (m, 1H, CH_{2P}), 3.47 - 3.35 (m, 1H, CHP), 2.75 - 2.66 (m, 1H, CH_{2P}). \\
\end{align*}
\]

\[\text{\textsuperscript{13}}C{\textsuperscript{1}H}\text{-APT NMR (75 MHz, C}_{6}D_{6}, 298 K): \delta 160.8 (dd, J_{C-P} = 6, 2, C_{q-py}), 149.5 (s, C_{2-py}), 139.7 - 127.8 (C_{Ph}+C_{Py}), 124.6 (d, J_{C-P} = 5, C_{Py}), 121.0 (d, J_{C-P} = 2, C_{Py}), 44.7 (t, J_{C-P} = 16, CHP), 32.1 (dd, J_{C-P} = 22, 17, CH_{2P}). \]

\[\text{\textsuperscript{31}}P{\textsuperscript{1}H}\text{NMR (121 MHz, C}_{6}D_{6}, 298 K): \delta 3.4 (d, J_{P-P} = 21, CHP), -19.9 (d, J_{P-P} = 21, CH_{2P}).\]

(Z)-2-(2-(diphenylphosphanyl)vinyl)pyridine (5e)

\[
\begin{align*}
\delta & 8.43 - 8.42 (m, 1H, H_{2-py}), 7.66 - 6.55 (13H, CH_{Ph}), 7.22 (overlapped, 1H, =CH). \\
\end{align*}
\]

\[\text{\textsuperscript{31}}P{\textsuperscript{1}H}\text{NMR (121 MHz, C}_{6}D_{6}, 298 K): \delta -15.0 (s).\]

(E)-2-(2-(diphenylphosphanyl)vinyl)pyridine (6e)

\[
\begin{align*}
\delta & 8.45 - 8.43 (m, 1H, H_{2-py}), 7.69 - 6.63 (13H, CH_{Ph}), 8.10 (dd, 1H, J_{H-H} = 17, J_{H-P} = 13, =CH), 7.08 (dd, 1H, J_{H-H} = 17, J_{H-P} = 11, =CH). \\
\end{align*}
\]

\[\text{\textsuperscript{31}}P{\textsuperscript{1}H}\text{NMR (121 MHz, C}_{6}D_{6}, 298 K): \delta -11.8 (s).\]
NMR spectra of the reaction crude.

Reaction conditions: 2-ethynylpyridine (0.2 mmol), Ph₂PH (0.4 mmol), 1a (0.005 mmol), of C₆D₆ (0.5 mL), 72 h at 80 °C.

¹H NMR (300 MHz, C₆D₆, 298 K)
$^{31}\text{P}^1\text{H}}$ NMR (121 MHz, C$_6$D$_6$, 298 K)

$^{13}\text{C}^1\text{H}}$-APT NMR (75 MHz, C$_6$D$_6$, 298 K)
Reaction of 1-nonine and diphenylphosphine.

nonane-1,2-diylbis(diphenylphosphine) (7f)

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K):} & \delta 7.54 - 6.86 (20H, CH\textsubscript{Ph}), 2.69 - 2.58 (m, 1H, CHP), 2.57 - 2.50 (m, 1H, CH\textsubscript{2}P), 2.31 - 2.21 (m, 1H, CH\textsubscript{2}P), 2.19 - 1.06 (12H, CH\textsubscript{2}), 0.96 (t, J\textsubscript{H-H} = 7, 3H, CH\textsubscript{3}). \\
\text{\textsuperscript{13}C(\textsuperscript{1}H)-APT NMR (75 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K):} & \delta 139.4 - 128.4 (C\textsubscript{Ph}), 33.0 (dd, J\textsubscript{C-P}= 15, 12, CHP), \delta 31.2 (dd, J\textsubscript{C-P} = 14, 10, CH\textsubscript{2}(C\textsubscript{3})), 30.9 (dd, J\textsubscript{C-P} = 17, 15, CH\textsubscript{2}P), \delta 27.1 (dd, J\textsubscript{C-P} = 10, 2, CH\textsubscript{2}(C\textsubscript{4})), 32.2 - 23.1 (CH\textsubscript{2}(C\textsubscript{5}-C\textsubscript{8})), 14.0 (s, CH\textsubscript{3}). \\
\text{\textsuperscript{31}P(\textsuperscript{1}H) NMR (121 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K):} & \delta -3.7 (d, J\textsubscript{P-P} = 22, CHP), -20.4 (d, J\textsubscript{P-P} = 22, CH\textsubscript{2}P).
\end{align*}
\]

(Z)-non-1-en-1-yldiphenylphosphine (5f)

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K):} & \delta 7.64 - 7.30 (10H, CH\textsubscript{Ph}), 6.26 (overlapped, 1H, =CH), 6.18 (overlapped, 1H, =CH), 2.07 (overlapped, 2H, CH\textsubscript{2}CH), 1.62-0.90 (overlapped, 13H, (CH\textsubscript{2})\textsubscript{5}CH\textsubscript{3}). \\
\text{\textsuperscript{31}P(\textsuperscript{1}H) NMR (121 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K):} & \delta -29.8 (s).
\end{align*}
\]

(E)-non-1-en-1-yldiphenylphosphine (6f)

\[
\begin{align*}
\text{\textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K):} & \delta 7.65 - 7.22 (10H, CH\textsubscript{Ph}), 6.37 (overlapped, 1H, =CH), 6.33 (overlapped, 1H, =CH), 2.51 (overlapped, 2H, CH\textsubscript{2}CH), 1.71-0.89 (overlapped, 13H, (CH\textsubscript{2})\textsubscript{5}CH\textsubscript{3}). \\
\text{\textsuperscript{31}P(\textsuperscript{1}H) NMR (121 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K):} & \delta -13.4 (s).
\end{align*}
\]
NMR spectra of the reaction crude.

Reaction conditions: 1-nonyne (0.2 mmol), Ph₂PH (0.2 mmol), 1a (0.005 mmol), C₆D₆ (0.5 mL), 48 h at 80 °C.

¹H NMR (300 MHz, C₆D₆, 298 K)
$^{31}$P($^1$H) NMR (121 MHz, C$_6$D$_6$, 298 K)

$^{13}$C($^1$H)-APT NMR (75 MHz, C$_6$D$_6$, 298 K)
**Reaction of cyclopropylacetylene and diphenylphosphine.**

(1-cyclopropylethane-1,2-diyl)bis(diphenylphosphine) (7g)

\[
\begin{array}{c}
\text{P} \\
\text{P} \\
\text{C} \\
\text{P} \\
\text{C} \\
\end{array}
\]

\[\text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H} \text{C} \text{H}
\]

\[\delta 7.66 - 6.87 (20H, \text{CH}_\text{Ph}), 2.74 - 2.64 (m, 1H, \text{CH}_2\text{P}), 2.48 - 2.37 (m, 1H, \text{CH}_2\text{P}), 2.08 - 1.96 (m, 1H, \text{CHP}), 0.96 - 0.84 (m, 1H, CH), 0.72 - 0.62 (m, 1H, CH), 0.62 - 0.52 (m, 1H, CH), 0.42 - 0.29 (m, 1H, CH), 0.10 - 0.01 (m, 1H, CH).
\]

\[\text{13C}^{1}\text{H}-\text{APT NMR (75 MHz, C}_6\text{D}_6, 298 K): \delta 139.3 - 128.2 (\text{C}_\text{Ph}), 38.9 (dd, J_{\text{C-P}} = 16, 12, \text{CHP}), 33.2 (dd, J_{\text{C-P}} = 19, 15, \text{CH}_2\text{P}), 15.2 (dd, J_{\text{C-P}} = 19, 5, \text{CH}), 7.5 (dd, J_{\text{C-P}} = 13, 8, \text{CH}_2), 5.9 (dd, J_{\text{C-P}} = 5, 3, \text{CH}_2).
\]

\[\text{31P}^{1}\text{H} \text{NMR (121 MHz, C}_6\text{D}_6, 298 K): \delta 0.3 (d, J_{\text{P-P}} = 23, \text{CHP}), -18.6 (d, J_{\text{P-P}} = 23, \text{CH}_2\text{P}).
\]

\[\text{(Z)-(2-cyclopropylvinyl)diphenylphosphine (5g)}
\]

\[\begin{array}{c}
\text{P} \\
\text{CH} \\
\text{C} \\
\text{C} \\
\end{array}
\]

\[\text{H NMR (300 MHz, C}_6\text{D}_6, 298 K): \delta 7.71 - 7.19 (10H, \text{CH}_\text{Ph}), 6.20 (dd, 1H, J_{\text{H-H}} = 12, J_{\text{H-P}} = 3, \text{CHP}), 5.61 (\text{overlapped}, 1H, =\text{CH}), 2.38 (\text{overlapped}, 1H, \text{CHCH}_2\text{H}_4), 0.65 (\text{overlapped}, 2H, \text{CH}_2), 0.35 (\text{overlapped}, 2H, \text{CH}_2).
\]

\[\text{31P}^{1}\text{H} \text{NMR (121 MHz, C}_6\text{D}_6, 298 K): \delta -29.3 (s).
\]

\[\text{(E)-(2-cyclopropylvinyl)diphenylphosphine (6g)}
\]

\[\begin{array}{c}
\text{P} \\
\text{C} \\
\text{C} \\
\end{array}
\]

\[\text{H NMR (300 MHz, C}_6\text{D}_6, 298 K): \delta 7.66 - 7.08 (10H, \text{CH}_\text{Ph}), 6.40 (dd, 1H, J_{\text{H-H}} = 16, J_{\text{H-P}} = 2, =\text{CHP}), 5.88 (\text{overlapped}, 1H, =\text{CH}), 1.43 (\text{overlapped}, 1H, \text{CHCH}_2\text{H}_4), 0.59 (\text{overlapped}, 2H, \text{CH}_2), 0.34 (\text{overlapped}, 2H, \text{CH}_2).
\]

\[\text{31P}^{1}\text{H} \text{NMR (121 MHz, C}_6\text{D}_6, 298 K): \delta -13.1 (s).
\]

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NMR spectra of the reaction crude.

Reaction conditions: cyclopropylacetylene (0.2 mmol), Ph₂PH (0.4 mmol), 1a (0.005 mmol), C₆D₆ (0.5 mL), 72 h at 80 °C.

¹H NMR (300 MHz, C₆D₆, 298 K)
Reaction of 3-dimethylamino-1-propyne and diphenylphosphine.

2,3-bis(diphenylphosphanyl)-N,N-dimethylpropan-1-amine (7i)

\[
\text{[Image of 2,3-bis(diphenylphosphanyl)-N,N-dimethylpropan-1-amine (7i)]}
\]

\[^1\text{H}\text{ NMR (300 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 7.73 - 7.02 (20\text{H, CH}_\text{Ph}), 2.87 - 2.78 (\text{m, } 1\text{H, CHP}), 2.78 - 2.69 (\text{m, } 1\text{H, CH}_2\text{N}), 2.62 - 2.54 (\text{m, } 2\text{H, CH}_2\text{P}), 2.54 - 2.48 (\text{m, } 1\text{H, CH}_2\text{N}), 2.13 (\text{s, } 6\text{H, CH}_3). \]

\[^{31}\text{P}\{^1\text{H}\}\text{ NMR (121 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -4.67 (\text{d, } J_{\text{P-P}} = 35, \text{ CHP}), -18.83 (\text{d, } J_{\text{P-P}} = 35, \text{ CH}_2\text{P}). \]

\[^{13}\text{C}\{^1\text{H}\}\text{-APT NMR (75 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 140.3 - 132.5 (\text{C}_\text{Ph}), 61.5 (\text{dd, } J_{\text{C-P}} = 15, 7, \text{ CH}_2\text{N}), 45.5 (\text{s, } \text{CH}_3\text{N}), 32.7 (\text{dd, } J_{\text{C-P}} = 16, 12, \text{ CHP}), 30.2 (\text{dd, } J_{\text{C-P}} = 17, 12, \text{ CH}_2\text{P}). \]

\[^{31}\text{P}\{^1\text{H}\}\text{ NMR (121 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -4.7 (\text{d, } J_{\text{P-P}} = 35, \text{ CHP}), -18.8 (\text{d, } J_{\text{P-P}} = 35, \text{ CH}_2\text{P}). \]

\[(Z)-3-\text{(diphenylphosphanyl)-N,N-dimethylprop-2-en-1-amine (5i)}\]

\[
\text{[Image of (Z)-3-\text{(diphenylphosphanyl)-N,N-dimethylprop-2-en-1-amine (5i)}]
\]

The NMR spectrum was consistent with that of the published data.\[^{10}\] \[^1\text{H}\text{ NMR (300 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 7.40 - 7.00 (10\text{H, CH}_\text{Ph}), 6.52 - 6.30 (\text{overlapped, m, } 2\text{H, PHC=CHC}), 2.90 - 2.78 (\text{m, } 2\text{H, CH}_2\text{N}), 2.12 (\text{s, } 6\text{H, CH}_3). \]

\[^{31}\text{P}\{^1\text{H}\}\text{ NMR (121 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -30.0 (\text{s}). \]

\[(E)-3-\text{(diphenylphosphanyl)-N,N-dimethylprop-2-en-1-amine (6i)}\]

\[
\text{[Image of (E)-3-\text{(diphenylphosphanyl)-N,N-dimethylprop-2-en-1-amine (6i)}]
\]

The NMR spectrum was consistent with that of the published data.\[^{10}\] \[^1\text{H}\text{ NMR (300 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta 7.57 - 6.93 (10\text{H, CH}_\text{Ph}), 6.49 - 6.23 (\text{overlapped, m, } 2\text{H, PHC=CHC}), 2.79 - 2.64 (\text{m, } 2\text{H, CH}_2\text{N}), 2.14 (\text{s, } 6\text{H, CH}_3). \]

\[^{31}\text{P}\{^1\text{H}\}\text{ NMR (121 MHz, C}_6\text{D}_6, 298 \text{ K): } \delta -13.8 (\text{s}). \]
NMR spectra of the reaction crude.

Reaction conditions: 3-dimethylamino-1-propyne (0.1 mmol), Ph₂PH (0.2 mmol),
1a (0.005 mmol), C₆D₆ (0.5 mL), 24 h at 120 °C.

¹H NMR (300 MHz, C₆D₆, 298 K)
$^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$, 298 K)

$^{13}$C{$^1$H}-APT NMR (75 MHz, C$_6$D$_6$, 298 K)
Reaction of 3,3-Dimethyl-1-butyne and diphenylphosphine.

(Z)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine (5h)

The NMR spectrum was consistent with that of the published data.\(^{[13]}\) \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\), 298 K): \(\delta\) 7.68 – 6.92 (10H, CH\(_{\text{Ph}}\)), 6.45 (dd, 1H, \(J_{\text{H-H}} = 28, J_{\text{H-P}} = 13\), CHC), 6.21 (dd, 1H, \(J_{\text{H-H}} = 13, J_{\text{H-P}} = 4\), CHP), 1.37 (s, 9H, C(CH\(_3\))\(_3\)).

\(^{31}\)P\(^{1}\)H\) NMR (121 MHz, CDCl\(_3\)): \(\delta\) -29.0 (s).

(E)-(3,3-dimethylbut-1-en-1-yl)diphenylphosphine (6h)

The NMR spectrum was consistent with that of the published data.\(^{[13]}\) \(^1\)H NMR (300 MHz, C\(_6\)D\(_6\), 298 K): \(\delta\) 7.71 – 6.89 (10H, CH\(_{\text{Ph}}\)), 6.52 (dd, 1H, \(J_{\text{H-H}} = 17, J_{\text{H-P}} = 16\), CHC), 6.37 (dd, 1H, \(J_{\text{H-H}} = 17, J_{\text{H-P}} = 4\), CHP), 1.02 (s, 9H, C(CH\(_3\))\(_3\)).

\(^{31}\)P\(^{1}\)H\) NMR (121 MHz, CDCl\(_3\)): \(\delta\) -13.3 (s).
NMR spectra of the reaction crude.

Reaction conditions: 3,3-Dimethyl-1-butyne (0.2 mmol), Ph₂PH (0.2 mmol), 1a (0.005 mmol), C₆D₆ (0.5 mL), 24 h at 80 °C.

¹H NMR (300 MHz, C₆D₆, 298 K)

³¹P{¹H} NMR (121 MHz, C₆D₆, 298 K)
Reaction of diphenylacetylene and diphenylphosphine.

(E)-(1,2-diphenylvinyl)diphenylphosphine (6j)

The NMR spectrum was consistent with that of the published data.[12] $^1$H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 7.57 – 6.87 (20H, CHPh) 6.78 (d, 1H, $J_{H-P}$ = 9, =CH).

$^{31}$P{$^1$H} NMR (121 MHz, C$_6$D$_6$, 298 K): δ 9.1 (s).
NMR spectra of the reaction crude.

Reaction conditions: diphenylacetylene (0.1 mmol), Ph$_2$PH (0.2 mmol), 1a (0.005 mmol), of tol-$d_8$ (0.5 mL), 24 h at 120 °C.

$^1$H NMR (300 MHz, C$_6$D$_6$, 298 K)

$^{31}$P($^1$H) NMR (121 MHz, C$_6$D$_6$, 298 K)
Preparation and isolation of diphosphine-borane adducts.

In a Young type NMR tube 0.005 mol of catalyst 1a were dissolved in 0.5 mL of toluene and then 0.2 mmol (35 μL) of Ph₂PH and 0.1 mmol of the corresponding alkyne were added and the solution was heated at 120 °C for 24 h. At the end of the reaction, the volatiles were removed in vacuo. The residue was dissolved in 1 mL of dichloromethane and filtered through a short pad of silica (2 cm). The resulted solution was treated with 0.32 mmol (30 μL) of BH₃-SMe₂ in a schlenk tube and the mixture magnetically stirred for 1h at room temperature. After the elimination of volatiles in vacuo the samples were dissolved in 2 mL of CH₃CN and then purified by HPLC operating in reverse phase. Samples were injected and eluted at 30°C with a mixture of acetonitrile:water (80:20) pumped at a flow rate of 15 mL/min. The elimination of volatiles in vacuo provides the diphosphine-borane adducts that were isolated as solids and characterized by NMR.
(1-(4-(trifluoromethyl)phenyl)ethane-1,2-diyl)bis(diphenylphosphine)-bis(borane) (7c-BH$_3$)

Yield: 20 mg (35%), off yellow solid. $^1$H NMR (500 MHz, CDCl$_3$, 298 K): δ 8.05 – 6.86 (m, 24H, CH$_2$Ph), 4.57 – 4.47 (m, 1H, CHP), 3.24 – 3.13 (m, 1H, CH$_2$P), 2.55 – 2.44 (m, 1H, CH$_2$P), 1.28 – 0.66 (br, 6H, BH$_3$). $^{13}$C($^1$H)-APT NMR (126 MHz, CDCl$_3$, 298 K): δ 137.2 – 123.3 (C$_{Ph}$), 125.9 (q, $J_{C-F}$ = 272 Hz, CF$_3$), 37.5 (d, $J_{C-P}$ = 30 Hz, CHP), 26.9 (dd, $J_{C-P}$ = 34, 5 Hz, CH$_2$P). $^{31}$P($^1$H) NMR (202 MHz, CDCl$_3$, 298 K): δ 25.0 (br, CHP), 17.0 (br, CH$_2$P). $^{11}$B($^1$H) NMR (160 MHz, CDCl$_3$, 298 K): δ -42.1 (br, BH$_3$), -40.3 (br, BH$_3$). HRMS (ESI) m/z calcd for C$_{33}$H$_{33}$B$_2$F$_3$P$_2$ (M + Na$^+$) 593.2099 found 593.2070
$7c$-$BH_3$: $^1$H NMR (500 MHz, CDCl$_3$, 298 K)
$7c$-$\text{BH}_3$: $^{13}\text{C}[^1\text{H}]$-APT NMR (126 MHz, CDCl$_3$, 298 K)
7c-BH$_3$: $^{31}$P($^1$H) NMR (202 MHz, CDCl$_3$, 298 K)

7c-BH$_3$: $^{11}$B($^1$H) NMR (160 MHz, CDCl$_3$, 298 K)
(1-(3-methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine)-bis(borane) (7d-BH₃)

Yield: 22 mg (42%), off white solid. ¹H NMR (500 MHz, CDCl₃, 298 K): δ 8.05 – 6.26 (m, 24H, CH₆Ph), 4.46 – 4.37 (m, 1H, CHP), 3.45 (s, 3H, OMe), 3.25 – 3.15 (m, 1H, CH₂P), 2.47 – 2.37 (m, 1H, CH₂P), 1.28 – 0.64 (br, 6H, BH₃). ¹³C{¹H}-APT NMR (126 MHz, CDCl₃): δ 135.8 – 111.9 (C₆Ph), 54.9 (s, OCH₃), 37.8 (dd, J_C-P = 30, 2 Hz, CHP), 27.0 (dd, J_C-P = 34, 6 Hz, CH₂P). ³¹P{¹H} NMR (202 MHz, CDCl₃, 298 K): δ 26.6 (br, CHP), 16.7 (br, CH₂P). ¹¹B{¹H} NMR (160 MHz, CDCl₃, 298 K): δ -41.6 (br, BH₃), -40.2 (br, BH₃). HRMS (ESI) m/z calcd for C₃₃H₃₆B₂O₃P₂ (M + Na⁺) 555.2331 found 555.2312
7d-BH$_3$: $^1$H NMR (500 MHz, CDCl$_3$, 298 K)
7d-BH₃: $^{13}$C{$^1$H}-APT NMR (126 MHz, CDCl₃, 298 K)
7d-BH$_3$: $^{31}$P($^1$H) NMR (202 MHz, CDCl$_3$, 298 K)

7d-BH$_3$: $^{11}$B($^1$H) NMR (160 MHz, CDCl$_3$, 298 K)
(nonane-1,2-diylbis(diphenylphosphine))-bis(borane) (7f-BH3)

Yield: 22 mg (42%), brown waxy solid. $^1$H NMR (500 MHz, CDCl3, 298 K): δ 7.85 – 7.18 (m, 20H, CHPh), 3.21 – 3.08 (m, 1H, CHP), 2.65 – 2.54 (m, 1H, CH2P), 2.21 – 2.11 (m, 1H, CH2P), 1.60 - 0.37 (m, 12H, CH2), 1.22-0.91 (br, 6H, BH3), 0.75 (t, $J_{H-H} = 7$ Hz, 3H, CH3). $^{13}$C($^1$H)-APT NMR (126 MHz, CDCl3, 298 K): δ 133.0 – 127.7 (CPh), 29.9 (d, $J_{C-P} = 2$ Hz, CH2(C3)), 29.3 (dd, $J_{C-P} = 33$, 2 Hz, CHP), 28.1 (d, $J_{C-P} = 3$ Hz, CH2(C4)), 27.2 (dd, $J_{C-P} = 33$, 5 Hz, CH2P), 31.5 – 22.5 (all s, CH2(C5-C8)), 14.1 (s, CH3). $^{31}$P($^1$H) NMR (202 MHz, CDCl3, 298 K): δ 25.0 (br, CHP), 17.0 (br, CH2P). $^{11}$B($^1$H) NMR (160 MHz, CDCl3, 298 K): δ -42.1 (br, BH3), -39.6 (br, BH3). HRMS (ESI) m/z calcd for C_{33}H_{44}B_{2}P_{2} (M + Na$^+$) 523.3020 found 523.3005
7f-BH₃: $^1$H NMR (500 MHz, CDCl₃, 298 K)
7f-BH$_3$: $^{13}$C($^1$H)-APT NMR (126 MHz, CDCl$_3$, 298 K)
7f-BH₃: $^{31}$P{$^{1}$H} NMR (202 MHz, CDCl₃, 298 K)

7f-BH₃: $^{11}$B{$^{1}$H} NMR (160 MHz, CDCl₃, 298 K)
(1-cyclopropylethane-1,2-diyl)bis(diphenylphosphine))-bis(borane)  (7g-BH₃)

Yield: 13 mg (28%), off white solid. $^1$H NMR (500 MHz, CDCl₃, 298 K): δ 7.95 – 7.19 (m, 20H, CH₆Ph), 2.99 – 2.89 (m, 1H, CH₂P), 2.75 – 2.63 (m, 1H, CHP), 2.25 – 2.14 (m, 1H, CH₂P), 0.69 – 0.61 (m, 1H, CH), 0.01 – (-0.06) (m, 1H, CH₂), (-0.12) – (-0.20) (m, 1H, CH₂), (-0.78) – (-0.86) (m, 2H, CH₂). $^{13}$C{$^1$H}-APT NMR (126 MHz, CDCl₃, 298 K): δ 133.3 – 126.9 (C₆Ph), 35.1 (d, $J_{C-P}$ = 34 Hz, CHP), 28.5 (dd, $J_{C-P}$ = 33, 7 Hz, CH₂P), 12.2 (d, $J_{C-P}$ = 4 Hz, CH), 6.4 (dd, $J_{C-P}$ = 2 Hz, CH₂), 5.9 (dd, $J_{C-P}$ = 13 Hz, CH₂). $^{31}$P{$^1$H} NMR (202 MHz, CDCl₃, 298 K): δ 24.8 (br, CHP), 16.5 (br, CH₂P). $^{11}$B{$^1$H} NMR (160 MHz, CDCl₃, 298 K): δ -42.6 (br, BH₃), -39.8 (br, BH₃). HRMS (ESI) m/z calcd for C₂₉H₃₆B₂P₂ (M + Na⁺) 489.2224 found 489.2213
$7g\text{-BH}_3$: $^1\text{H NMR (500 MHz, CDCl}_3$, 298 K)
7g-BH₃: $^{13}$C($^1$H)-APT NMR (126 MHz, CDCl₃, 298 K)
7g-BH$_3$: $^{31}$P{$^1$H} NMR (202 MHz, CDCl$_3$, 298 K)

\[ \text{Graph of } 7g-BH_3: ^{31}P{^1}H \text{ NMR (202 MHz, CDCl}_3, 298 K) \]

7g-BH$_3$: $^{11}$B{$^1$H} NMR (160 MHz, CDCl$_3$, 298 K)

\[ \text{Graph of } 7g-BH_3: ^{11}B{^1}H \text{ NMR (160 MHz, CDCl}_3, 298 K) \]
(2,3-bis(diphenylphosphanyl)-N,N-dimethylpropan-1-amine)-tris(borane) (7i-BH₃)

Yield: 13 mg (26%), off white solid. $^1$H NMR (500 MHz, CDCl₃, 298 K): δ 7.91 – 7.05 (m, 20H, CH₆Ph), 3.77 – 3.65 (m, 1H, CHP), 3.32 – 3.23 (m, 1H, CH₂N), 3.03 – 2.93 (m, 1H, CH₂N), 2.81 – 2.62 (m, 2H, CH₂P), 2.0 (s, 3H, CH₃), 1.9 (s, 3H, CH₃). $^{13}$C$[^1$H]-APT NMR (126 MHz, CDCl₃, 298 K): δ 134.4 – 125.0 (C₆Ph), 65.0 (dd, $J_{C-P} = 9$, 3 Hz, CH₂N), 50.5 (s, CH₃N), 50.4 (s, CH₃N), 28.6 (dd, $J_{C-P} = 32$, 5 Hz, CH₂P), 26.2 (dd, $J_{C-P} = 32$, 2 Hz, CHP). $^{31}$P$[^1$H] NMR (202 MHz, CDCl₃, 298 K): δ 29.4 (s, CHP), 16.7 (s, CH₂P). $^{11}$B$[^1$H] NMR (160 MHz, CDCl₃, 298 K): δ -8.2 (br, N-BH₃), -42.5 (br, P-BH₃), -39.8 (br, P-BH₃). HRMS (ESI) m/z calcd for C₂₉H₄₀B₃NP₂ (M + Na⁺) 520.2822 found 520.2807
`7i-BH₃`: $^1$H NMR (500 MHz, CDCl₃, 298 K)
7i-BH$_3$: $^{13}$C$^{1}$H-APT NMR (126 MHz, CDCl$_3$, 298 K)
$7i$-$BH_3$: $^{31}P\{^1H\}$ NMR (202 MHz, CDCl$_3$, 298 K)

$7i$-$BH_3$: $^{11}B\{^1H\}$ NMR (160 MHz, CDCl$_3$, 298 K)
References:
11 O. T. Beachley, Jr., D. J. MacRae, A. Y. Kovalevsky, *Organometallics* 2003, **22**, 1690.