Supporting Information for:
A Bench-Stable Copper Photocatalyst for the Rapid Hydrophosphination of Activated and Unactivated Alkenes

Steven G. Dannenberg and Rory Waterman*
Department of Chemistry, University of Vermont, Burlington, Vermont 05405-0125, United States
* Rory.Waterman@uvm.edu

Contents

General Information

All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques unless otherwise noted. $CDCl_3$ was purchased and then degassed and dried over calcium hydride and then distilled and stored over 3 and 4 Å molecular sieves. Diphenylphosphine was synthesized according to literature procedures and stored under an inert atmosphere of N_2 prior to use.[1] Compounds **10**[2] was synthesized according to literature procedures. All other reagents were acquired from commercial sources and dried by conventional means, as necessary. ESI-mass spectra were collected on an AB-Sciex 4000 QTrap Hybrid Triple Quadrupole/Linear Ion trap mass spectrometer. ^1H, ^2H, ^{13}C, ^{31}P, $^{31}P\{^1H\}$ and ^{31}P HMBC NMR spectra were recorded at 25 °C with a Bruker AXR 500 MHz or Varian 500 MHz spectrometer.

Safety note: Phosphines are toxic, and many primary phosphines are volatile. Redox reactions or metal catalysts have the potential for rapid hydrogen evolution from phosphine substrates. Appropriate precautions for toxic gases and hydrogen are necessary in this work.

Resonances in ^1H NMR spectra are referenced to the residual solvent resonance ($CDCl_3$ = δ 7.28) or tetramethylsilane (TMS, δ 0.0). Reported $^{31}P\{^1H\}$ NMR resonances are relative to external 85% H_3PO_4. Spectral data for hydrophosphination products is consistent with literature reports.[1, 3-10] Previously unreported products were purified by silica gel column chromatography silica gel column chromatography with a 3:1 hexanes: DCM liquid phase in an M. Braun glovebox.

$CDCl_3$ is not visible in many of the spectra due to overlap with aromatic resonances of starting materials and products. The signal for acetylacetone is present in all catalytic reactions with **1** and is denoted by (ǂ) in the first catalytic hydrophosphination spectra of styrene and phenylphosphine in this document and then is not labeled in subsequent spectra. P-H bonds of some secondary phosphines are not visible in the crude spectra due to interaction with copper, but peaks become visible with the removal of copper by silica gel chromatography. Starting phosphines $PhPH_2$ and Ph_2PH signals are at approximately - 122 and - 40 ppm in the $^{31}P\{^1H\}$ NMR spectra and are not labeled.

Table S1. Symbols for products in spectra:

Single addition hydrophosphination product	*
Double addition hydrophosphination product	**
Ph_2P-PPh_2	†
PhHP-PHPh	††
Acetylacetone	ǂ
Internal standard of 1,3,5-trimethoxybenzene, ferrocene or tetramethylsilane	TMB, Fc, TMS (not labeled in all spectra; exists at δ 0)
External standard of PPh_3	ES or E.S. PPh_3

Aromatic peaks and most overlapping peaks are not indicated

General Procedure for catalytic experiments

In an N_2 filled dry box, 0.76 mmol of phosphine (or 0.38 mmol where applicable) and 0.38 mmol of unsaturated substrate (and internal or external standard where applicable) were measured and mixed in 0.6 mL $CDCl_3$. This solution was either pipetted into a shell vial containing 0.019 mmol of catalyst in 100 µL of $CDCl_3$ or catalyst was added via stock solution. The resulting solution was quickly transferred to either an aluminum foil wrapped J-Young type polytetrafluoroethylene-valved NMR tube or an NMR tube with a disposable NMR cap which was subsequently wrapped with parafilm. Neat reactions were added directly to a J-Young type NMR tube. For reactions containing an external standard, a sealed capillary containing 5 mg of PPh_3 was added to the NMR tube before capping. Upon removal from dry box, the outside of the tube was washed with a 50:50 water: bleach to remove trace amounts of malodorous phosphine on the outside of the tube. An initial ^1H and $^{31}P\{^1H\}$ NMR spectra was then obtained as soon as possible. After the initial NMR spectra, reactions were removed from the aluminum foil and placed in a photoreactor containing a Rexim G23 UV-A (9W) lamp (unless otherwise noted) at ambient temperature and shielded from external light. The temperature of the 360 nm photoreactor was measured to be 25–30 °C, depending on how long it had been in use. No efforts to control the temperature between this range were undertaken. Periodic ^1H and $^{31}P\{^1H\}$ NMR spectra were collected. Conversions were determined by integration of ^1H and $^{31}P\{^1H\}$ NMR spectra to starting materials and in many cases (see note below) confirmed by internal standard of either 1,3,5-trimethoxy benzene,[11] tetramethyl silane, or an external standard of PPh_3.

Note on the determination of conversions

Initial tests of reactivity were performed on all substrates, and conversions were determined by integration of product signals to starting material in the ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra. There was good agreement between ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra, and this method has precedent in catalytic hydrophosphination. [5, 6, 12, 13, 14, 15, 16, 17, 18,] To ensure the accuracy of this method, reactions from each class of substrates (styrenes, unactivated alkenes, alkynes, primary phosphines, secondary phosphines, etc.) were replicated with an internal standard of 1,3,5-trimethoxybenzene,[19] or TMS for ^{1}H NMR spectra or an external standard (sealed capillary) of PPh_3 For $^{31}P\{^{1}H\}$ NMR spectra.

For reactions between phenylphosphine and styrene, integration of product signals relative to a 1,3,5-trimethoxybenzene internal standard resulted in the same yield as integrating the starting materials to the products. Integration to an internal standard of TMS gave conversion *greater than 100%*. Thus, we had more confidence in the more conservative estimate of conversion obtained by our initial method.

Integration of product signals relative to a 1,3,5-trimethoxybenzene internal standard resulted in comparable conversions for the products of hydrophosphination of phenylphosphine with *p*-methylstyrene, and 1-hexene. At that point we were satisfied that our initial method of determining yield was satisfactory for primary phosphines and alkenes.

For reactions between diphenylphosphine and *p*-tertbutyl styrene there was good agreement our initial trial and a trial with 1,3,5-trimethoxybenzene. However, there was some discrepancy between the two methods in reaction between styrene and diphenylphosphine. There is some precedent for inconsistent behavior of styrene in hydrophosphination reactions.[3] Conversions determination by integration relative to the 1,3,5-trimethoxybenzene internal standard results in a *higher* and *less* accurate yield than by relative integration. It appears that the internal standard interacts with copper and the two ^{1}H NMR signals of 1,3,5-trimethoxybenzene did not integrate in the correct 3:1 ratio and exhibited splitting (see figure 1 below), and internal standard protons exhibited splitting based on interaction with phosphorus in a ^{31}P HMBC spectrum. This is surprising and not yet fully understood.

Finally, ferrocene was used as a standard. There was still variability in the results, and ferrocene appeared to inhibit the catalysis.

Overall, we have sought the most accurate conversion data, which was not merely a function of a single integration standard. As needed, we have often reported lower conversion based on mitigating factors with various standards.

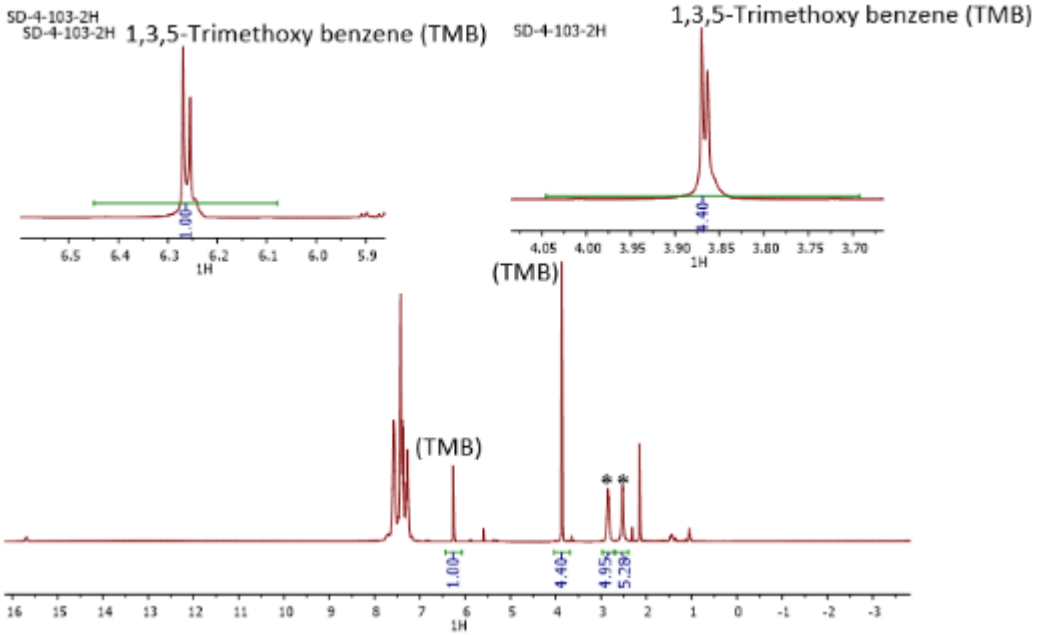


Figure S.1. Splitting of 1,3,5-trimethoxy benzene protons observed in ^{1}H NMR spectra of a catalytic reaction of styrene and phenylphosphine.

Spectral distribution of Rexim G23 UV-A (9W) lamp

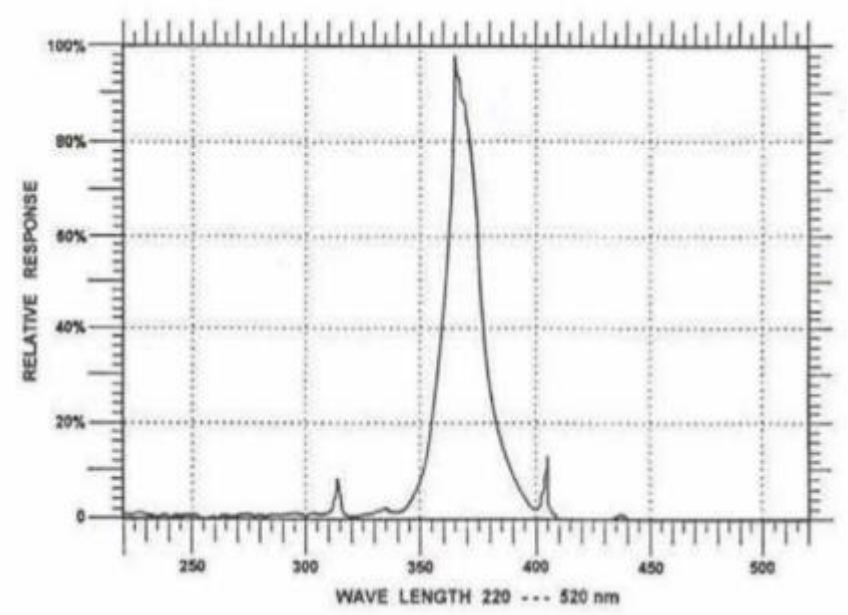


Figure S.2. Spectral distribution of Rexim G23 UV-A (9W) lamp as provided by manufacturer.

Photographs of the photoreactor

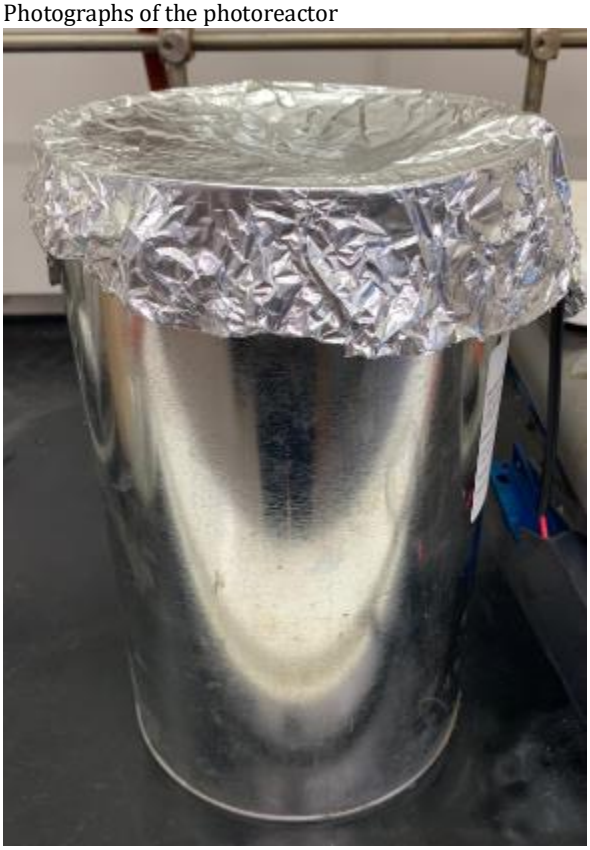


Figure S.3. Outside of the photoreactor containing a UV-A lamp

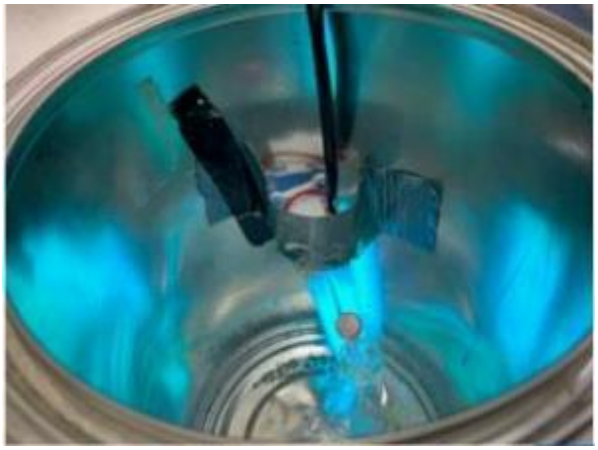
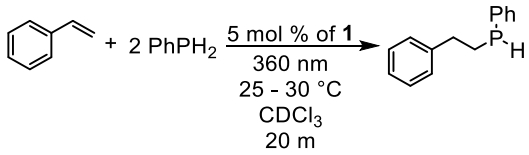


Figure S.4. Photograph of the inside of the photoreactor containing a UV-A lamp

Optimization of Conditions

Table S2.



Entry	Deviation from standard conditions	Conversion (%)
1	None	100
2	1 eq $PhPH_2$	51
3	Control; without **1,** 360 nm	6
4	Ambient light, 60 °C	59
5	Visible Light LED	45
6	Ambient light	15
7	Dark	7
8	2 mol % of **1**	100
9	1 mol % of **1**	90
10	25 mol % of **1**	40
11	Neat	100
12	Benzene-d_6 solution	100

Standard condition: 0.38 mmol (39.5 mg) of styrene and 0.76 mmol phenylphosphine (83.5 mg) and 0.19 mmol (5 mg) of **1** in 600 µL of $CDCl_3$. Changes in catalyst loading and phenylphosphine equivalents are with respect to styrene. Conversion to both secondary and tertiary phosphine determined by integration of ^1H and $^{31}P\{^1H\}$ NMR spectra.
The LED light bulb is a visible light 9 W, 800 Lumens 120 V, 60 Hz, 150 mA bulb

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Light dependence of hydrophosphination of styrene with phenylphosphine by **1**

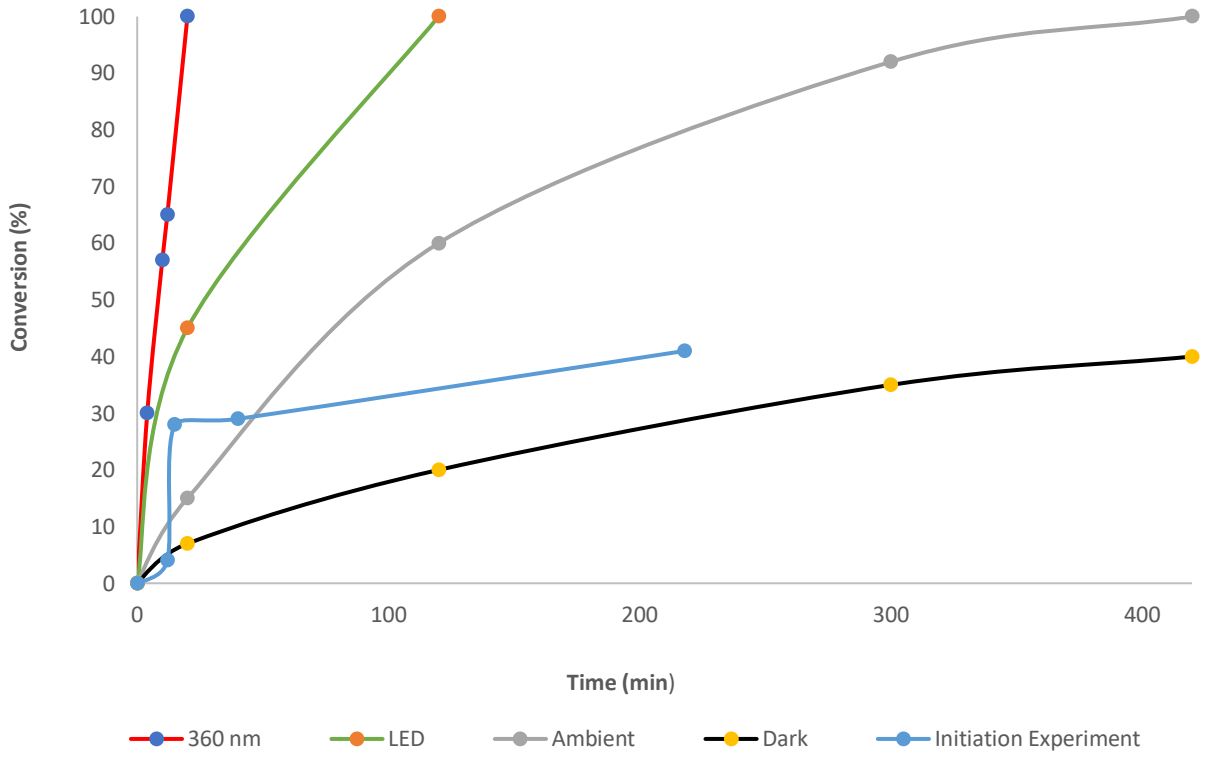
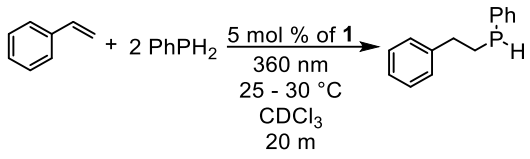


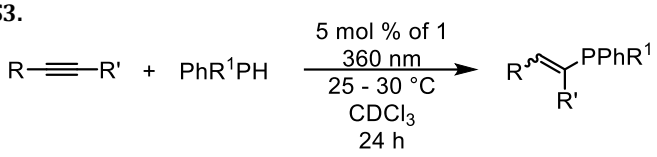
Figure S.5.

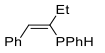
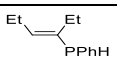
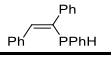
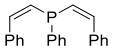
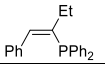
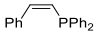
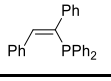


Note: The LED light bulb is a visible light 9 W, 800 Lumens 120 V, 60 Hz, 150 mA bulb

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

TABLE S3.



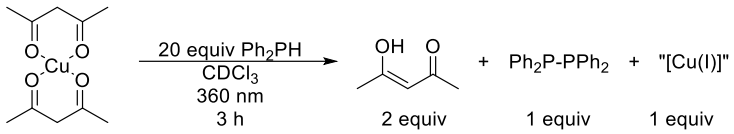
entry	R	R'	RR'PH	Major Product[a]	Conversion %[b]	*Z*:*E*
1	Ph	Et	$PhPH_2$		80	3:1
2	Ph	Et	2 $PhPH_2$		99	2.45:1
3	Et	Et	$PhPH_2$		48	1:1.7
4	Et	Et	2 $PhPH_2$		71	1:1.5
5	Ph	Ph	$PhPH_2$		40	1.9:1
6	Ph	Ph	2 $PhPH_2$		58	2.1:1
7	Ph	H	2 $PhPH_2$		86[c, d]	3:1[e]
8	Ph	H	0.5 $PhPH_2$		88[c, f]	2.7:1[e]
9	Ph	Et	Ph_2PH		74	4.8:1
10	Ph	H	Ph_2PH		41	32:1
11	Ph	H	2 Ph_2PH		77	37.5:1
12	Ph	Ph	Ph_2PH		12	1:0
13[g]	Ph	Ph	Ph_2PH		11	10:1
14	Ph	Ph	2 Ph_2PH		19[d](36[h])	35:1[h]

Conditions: 0.38 mmol of alkyne and 0.38 or 0.76 mmol of $PhPH_2$ or Ph_2PH and 0.019 mmol **1** [a] only the major stereoisomer is depicted [b] conversion to anti-markovnikov vinyl phosphine as determined by integration of ^1H and $^{31}P\{^1H\}$NMR spectra [c] double P-H bond activation product [d] 20 h [e] ratio of *Z,Z:E,Z* product [f] 1 h [g] 5 mol % of PPh_3 added [h] 72 h

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Reactions of **1** with Ph_2PH

In an N_2 filled dry box, 0.38 mmol (70.7 mg) of diphenylphosphine, 0.019 mmol (5 mg) of **1**, 6.6 mg (0.039 mmol) of 1,3,5-trimethoxybenzene as an internal standard, and a closed capillary containing 5 mg of PPh_3 in 50 µL of $CDCl_3$ as an external standard were measured and mixed in 0.8 mL in a J-Young type polytetrafluoroethylene-valved NMR tube wrapped in aluminum foil until an initial ^1H and $^{31}P\{^1H\}$ NMR spectra was obtained. The reaction was then placed under 360 nm irradiation and monitored periodically by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.



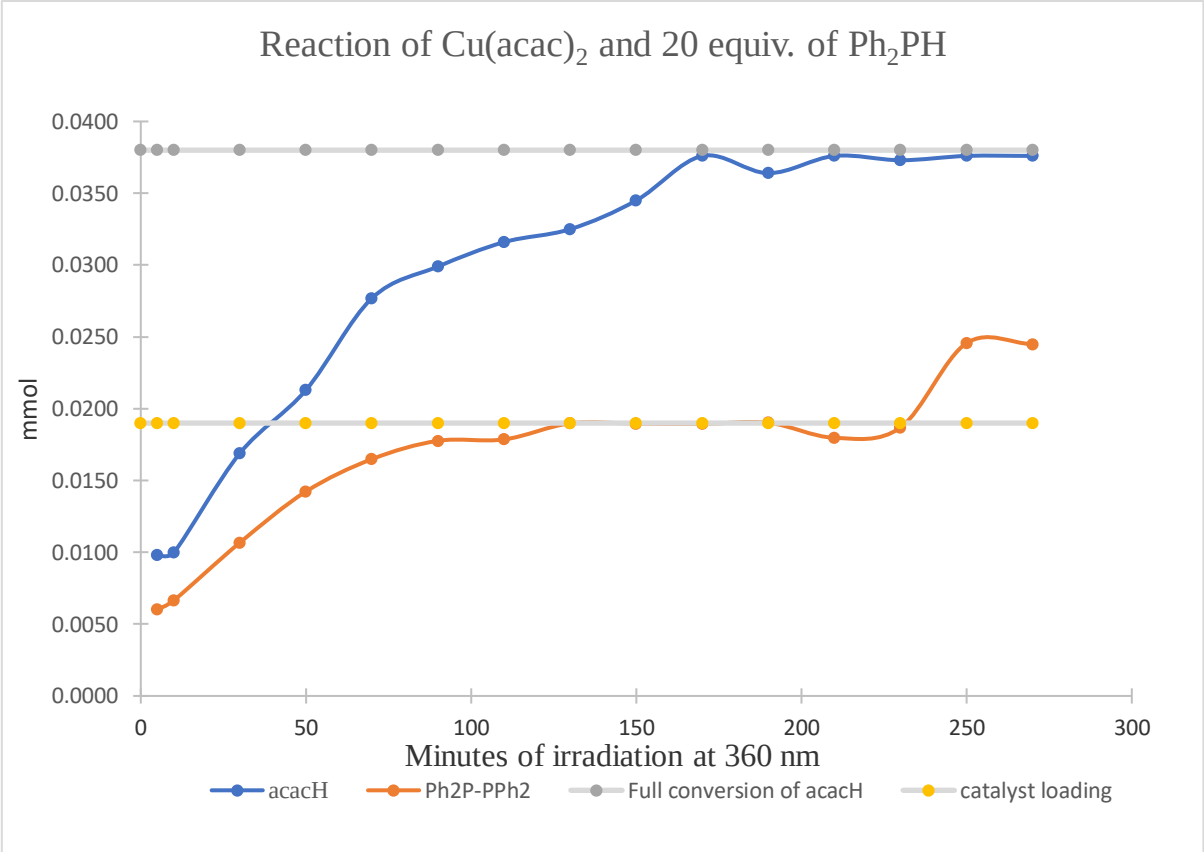


Figure S.6. Reaction of $Cu(acac)_2$ and 20 equiv. of Ph_2PH

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Reaction of **1** with 20 equiv. of Ph_2PH - replication in toluene

In an N_2 filled dry box, 0.38 mmol (70.7 mg) of diphenylphosphine, 0.019 mmol (5 mg) of **1**, in 500 µL of Toluene in 0.8 mL in a J-Young type polytetrafluoroethylene-valved NMR tube a $^{31}P\{^1H\}$ NMR spectra was obtained.

These spectra provide evidence for a phosphido species of unknown speciation. A singlet integrating to 5% of the phosphorus in solution at -31.9 in addition to the free Ph_2PH. The signal remained a singlet in the coupled ^{31}P NMR and is coupled only to aromatics in a ^{31}P HMBC spectra. Our attempts at crystalizing a discreet intermediate from these solutions resulted only in powders that were insoluble in common organic solvents.

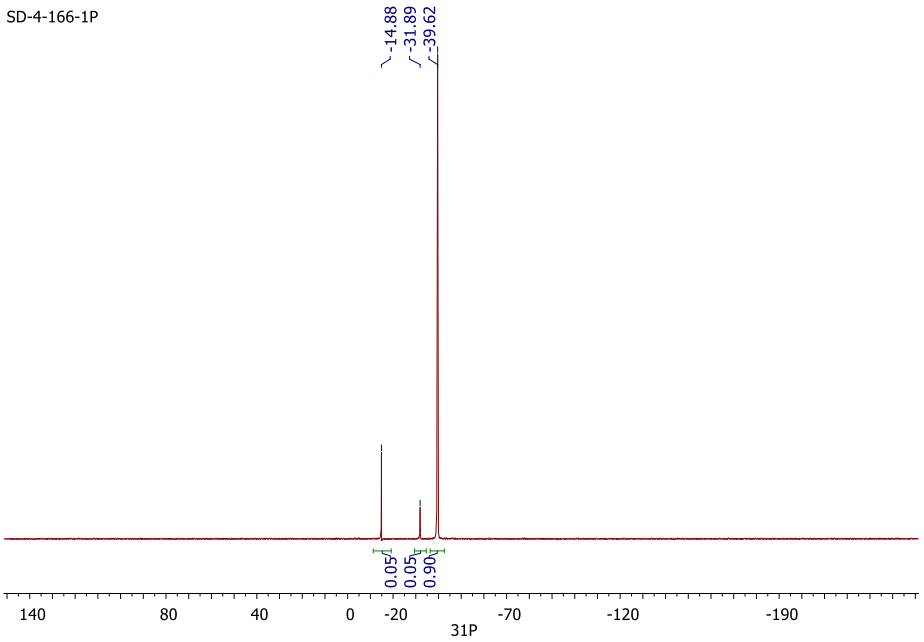


Figure S.7 ^{31}P NMR spectra (toluene, 202 MHz)

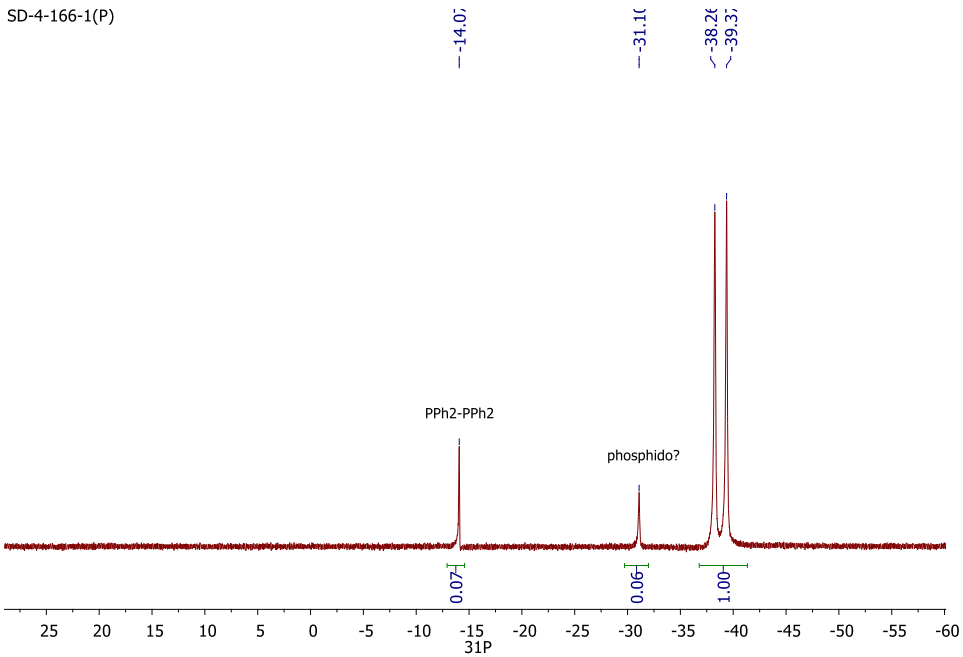


Figure S.8. $^{31}P\{^1H\}$ NMR spectra (toluene, 202 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Reaction of **1** with 20 equiv. of Ph_2PH - replication in toluene (continued)

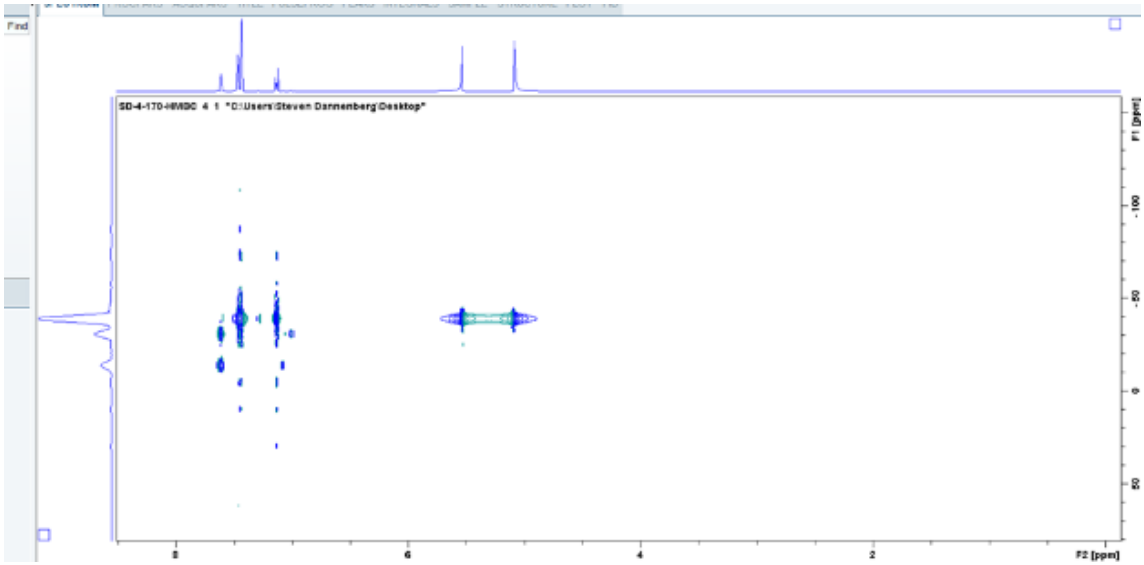


Figure S.9. ^{31}P HMBC NMR spectra (toluene d_8, 202 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Treatment of **1** with 1, 2, 4, 8, and 20 equiv. of Ph_2PH

In an N_2 filled dry box, 15 mg (0.057 mmol) of **1** was measured and mixed in ~0.6 mL $CDCl_3$ and transferred to a J-Young type polytetrafluoroethylene-valved NMR tube or an NMR tube. For the reaction with 20 equiv. of Ph_2PH only 5 mg of **1** was used. The corresponding equiv. of Ph_2PH were added by micropipette to the NMR tube and an initial ^1H and $^{31}P\{^1H\}$ NMR spectra was obtained.

Caulton reported $[(Ph_2PH)CuPPh_2]_n$ from the addition of multiple equivalents of Ph_2PH to $Cu(O^tBu)_4$.[20] Compound **1,** when treated with 2, 4, 8 and 20 equiv. of Ph_2PH in $CDCl_3$ solution, provided spectroscopic data consistent with observations made of $[(Ph_2PH)CuPPh_2]_n$. When compound **1** was treated with two equivalents of Ph_2PH a doublet with J_{PH} = 308 Hz was observed in the ^1H NMR spectra, which compares favorably to the literature report of 300 Hz reported by Caulton with $Cu(O^tBu)_4$. With both compounds, the doublet splitting decreases toward the value of free Ph_2PH (219 Hz) as additional Ph_2PH is present in solution. An additional similarity with the literature report was observed in the $^{31}P\{^1H\}$ NMR spectra where the signal was shifted downfield when one equivalent of diphenylphosphine was added and the signal shifted back upfield toward the value of free diphenylphosphine as more Ph_2PH was added to the solution. This behavior is indicative of exchange between free Ph_2PH, coordinated Ph_2PH, and likely a phosphido species and is a weighted average of the shifts and coupling constants.

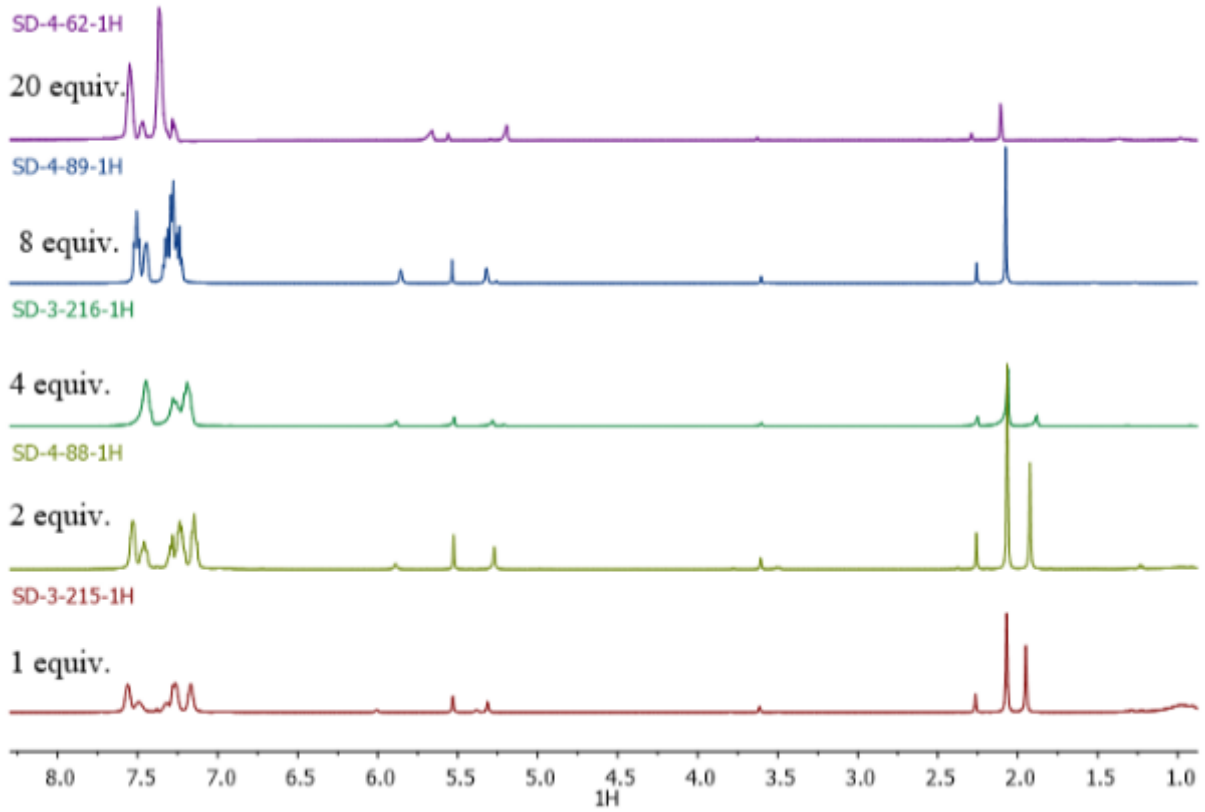


Figure S.10. Stacked ^1H NMR spectra ($CDCl_3$, 500 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Treatment of **1** with 1, 2, 4, 8, and 20 equiv. of Ph_2PH (continued)

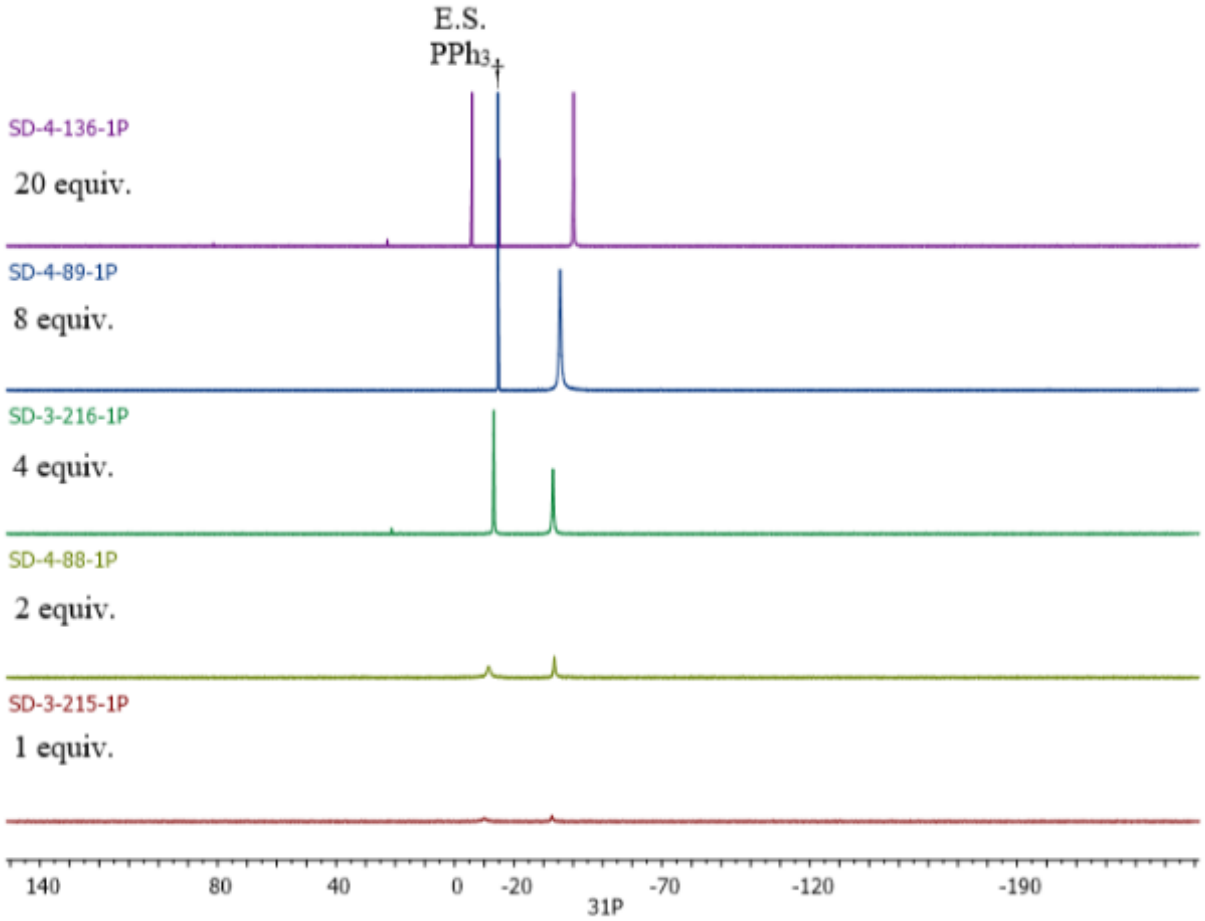


Figure S.11. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of styrene
Eqn (1)

Prepared in accordance with the general procedure with two equiv. of phenylphosphine**.** In an N_2 filled dry box, 0.76 mmol of phenylphosphine (83.5 µL, 83.5 mg) and 0.38 mmol of styrene (39.5 mg) were mixed in 0.5 mL of$CDCl_3$. This solution was then pipetted into a 4 ml shell vial containing 5 mg (0.0019 mmol) **1** in 100 µL $CDCl_3$. The resulting yellow solution was quickly transferred to an NMR tube, capped with a disposable NMR cap, parafilm was wrapped around the NMR cap, and the reaction was shielded from ambient light. After initial ^1H and $^{31}P\{^1H\}$ NMR spectra were obtained, the reaction was irradiated with 360 nm light and monitored every 10 min. The yellow solution faded over time to a clear solution. After 10 min of irradiation both the ^1H and $^{31}P\{^1H\}$ NMR spectra indicated 74% yield of secondary phosphine. After 20 min of irradiation, 100% of styrene was converted with 98:4:2 selectivity for the secondary hydrophosphination product compared to the PhHP-PHPh and tertiary products as measured by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Together, these indicate a 96% conversion of styrene to secondary phosphine phenyl(2-phenylethyl)phosphine ($PhPHCH_2CH_2Ph$).

Two subsequent trials conducted with an internal standard of 1,3,5-trimethoxybenzene resulted in 95% conversion and 87% conversion to secondary phosphine product $PhPHCH_2CH_2Ph$.

$^{31}P\{^1H\}$ NMR signals for the products in the crude reaction mixtures are broad due to interaction with paramagnetic copper and sharpen upon removal of copper by filtering the crude residue through a plug of silica and evaporation of the volatile species by vacuum. Separation of secondary, tertiary and dehydrocoupled products can be achieved by silica gel column chromatography with a 3:1 hexanes: DCM liquid phase. 54 mg (0.25 mmol, 66% yield) of phenyl(2-phenylethyl)phosphine ($PhPHCH_2CH_2Ph$) was isolated. Spectra are consistent with previous reports.[6]

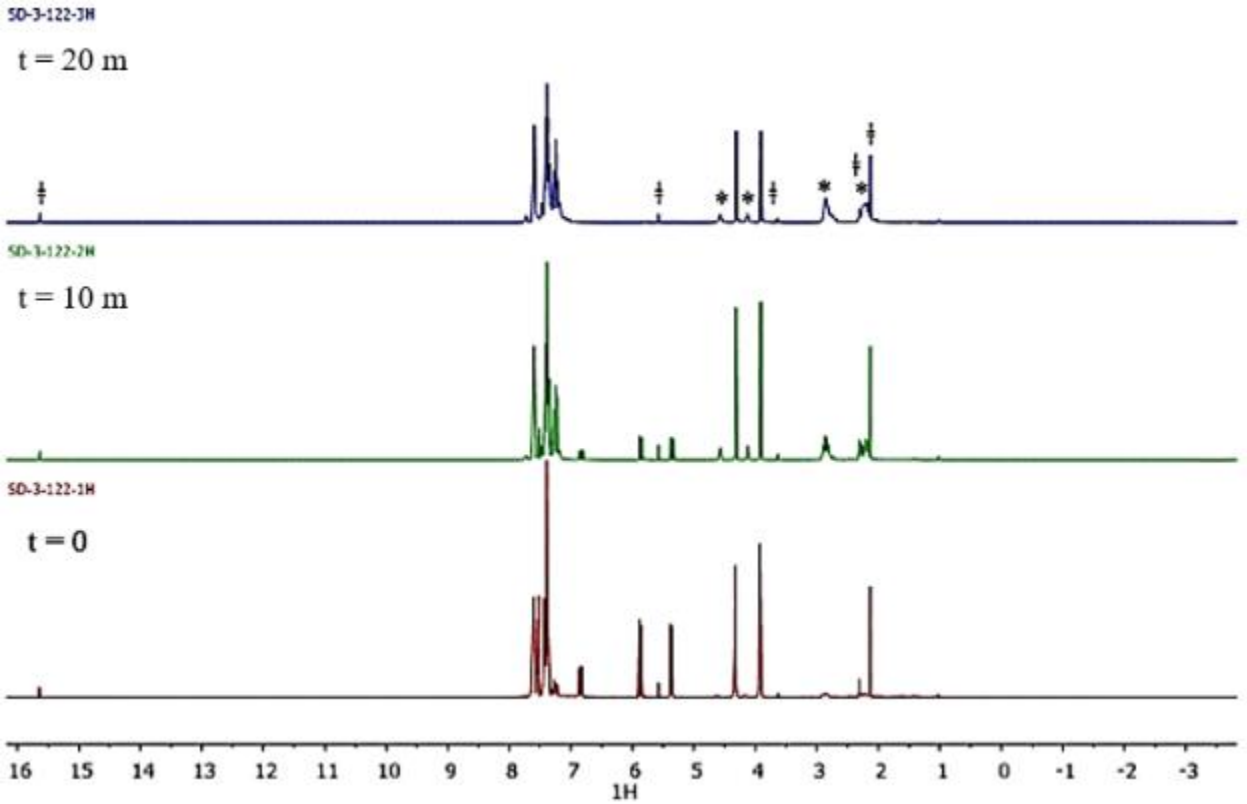
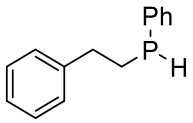


Figure S.12. Stacked ^1H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of styrene with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

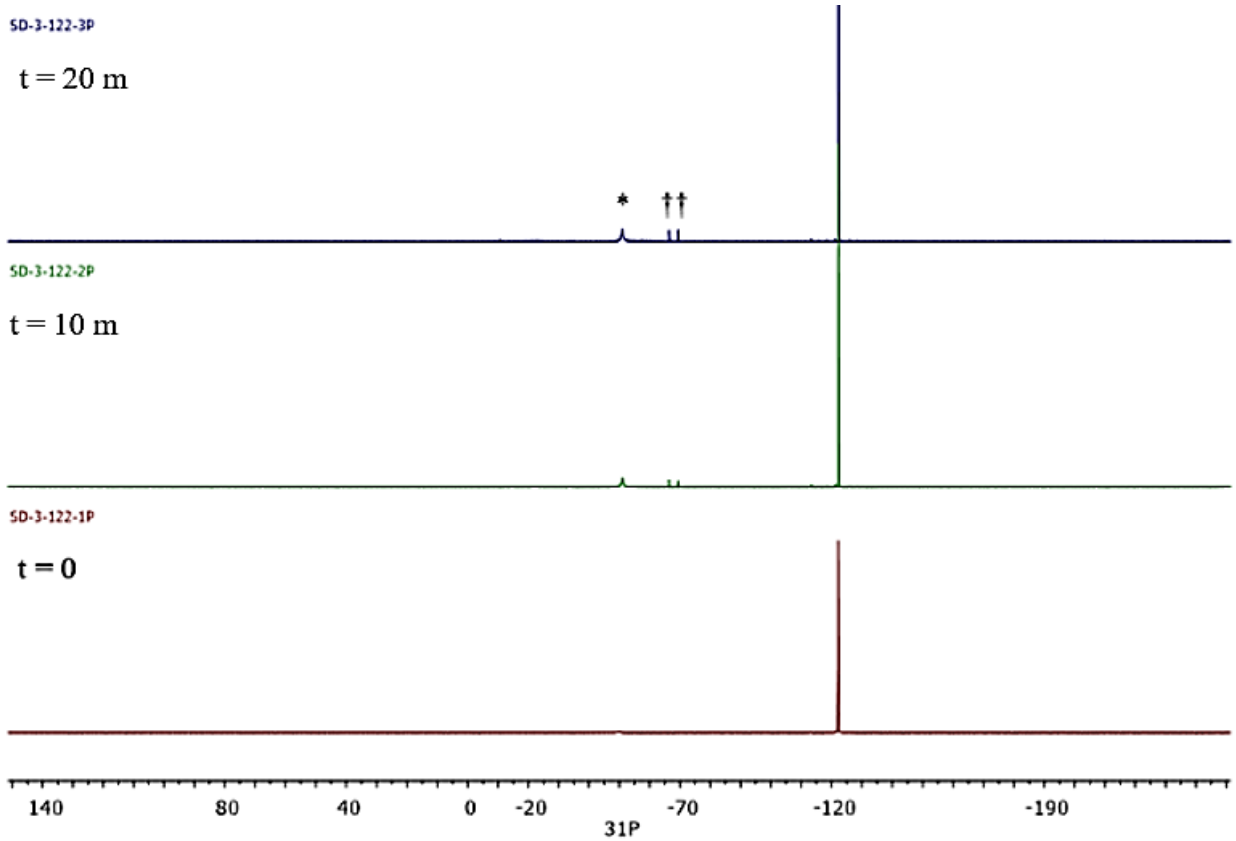
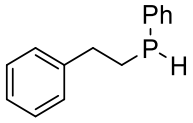


Figure S.13. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of styrene with two equiv. of phenylphosphine by 5 mol % of 1 under 360 nm irradiation (continued)

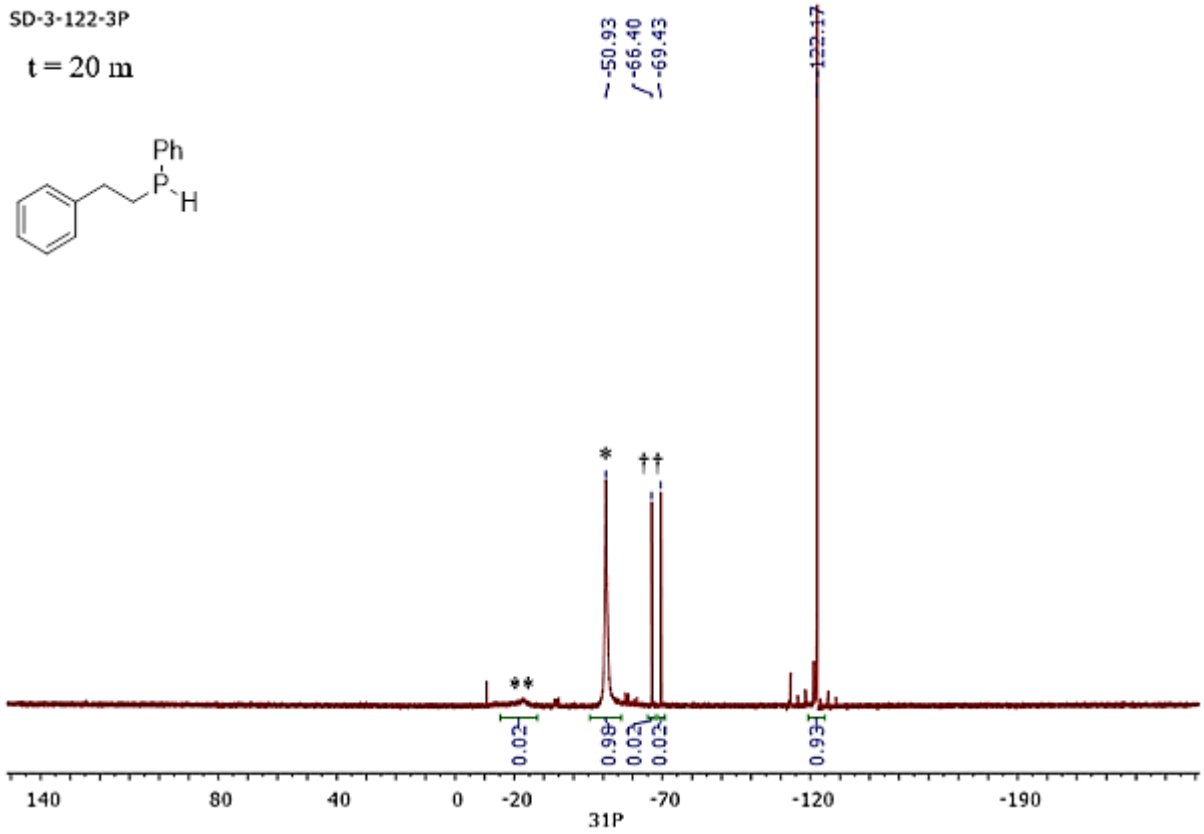


Figure S.14. $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz) at t = 20 min of 360 nm irradiation

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of styrene with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (Trial 2)

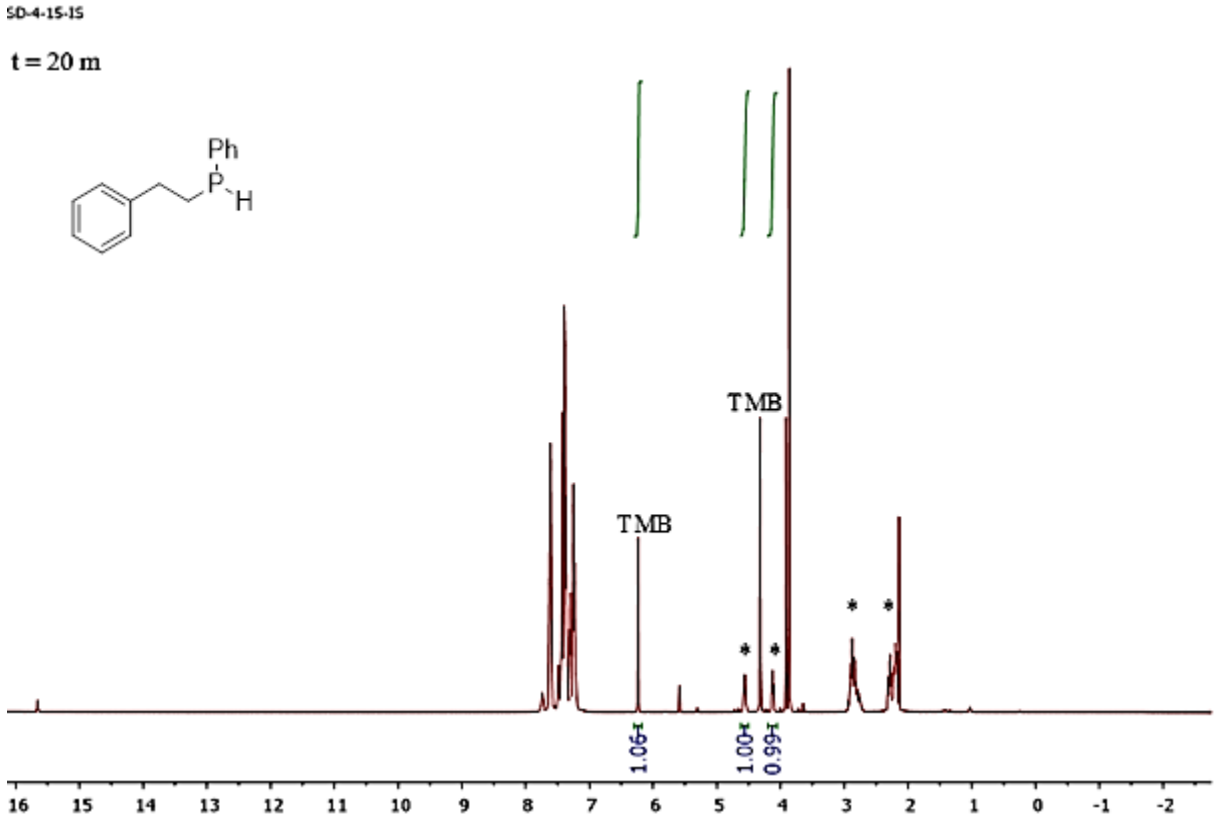


Figure S.15. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) at t = 20 min of 360 nm irradiation

Internal standard yield calculation: (1.99/(1.06/3)) * (0.0108 g/168.19 g/mol) / 0.38 mmol = 95% yield of secondary phosphine

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of styrene with two equiv. of phenylphosphine with 5 mol % of **1** under 360 nm irradiation (continued)

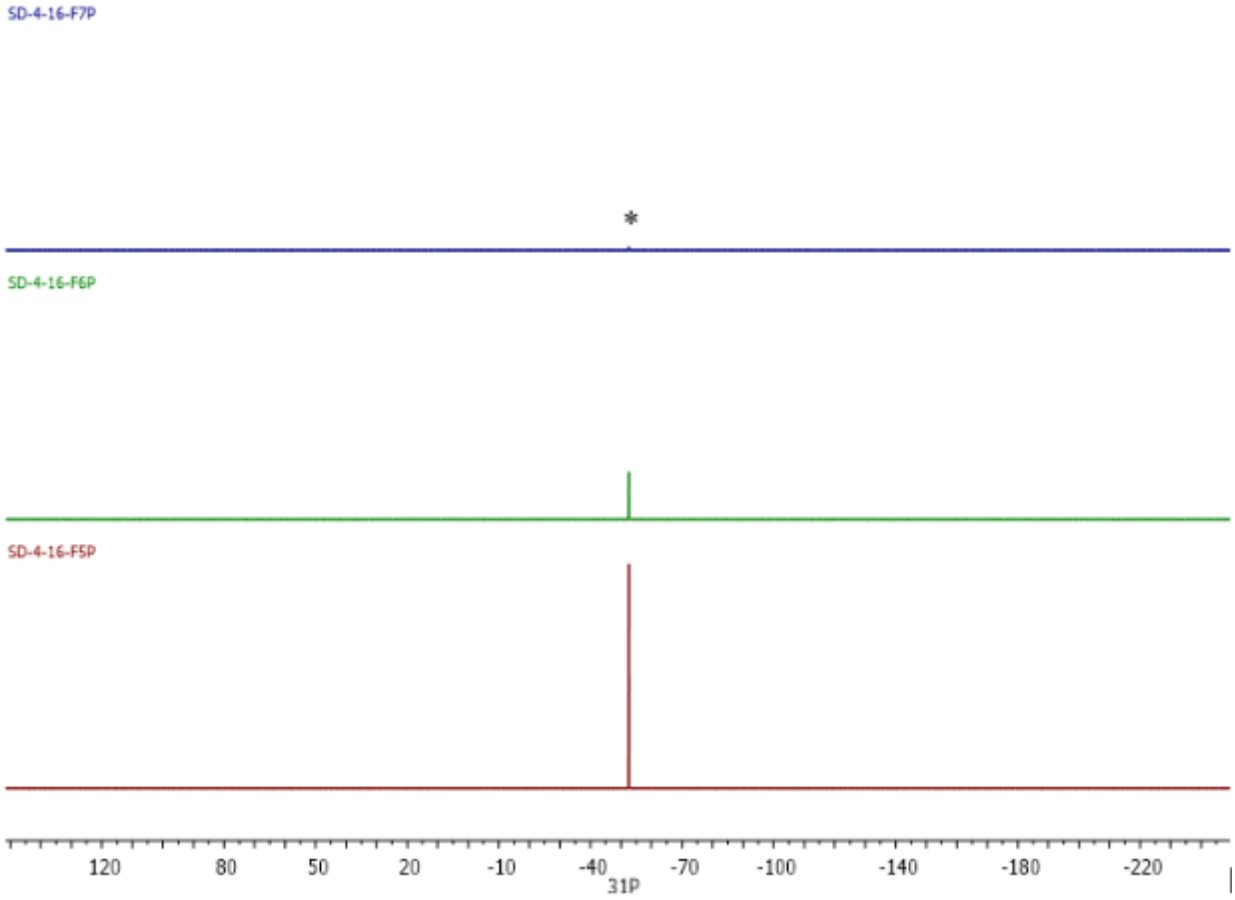
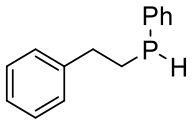


Figure S.16. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz) of three isolated fractions from trial 3. 0.54 grams (0.25 mmol) phenyl(2-phenylethyl)phosphine was recovered from fractions 5,6 and 7. Yield calculation: 35.5 mg + 15.3 mg + 3.2 mg = (0.054 g / 214.25 g/mol)/0.00038 mol = 66% yield



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of styrene with one equiv. of diphenylphosphine by **1**
Eqn (2)

Prepared according to the general procedure with one equiv. of diphenylphosphine and 11.5 mg (0.068 mmol) of 1,3,5- trimethoxybenzene an internal standard. 100% conversion of styrene was measure after 5 h of 360 nm irradiation as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra is in accordance with previous reports.[21]

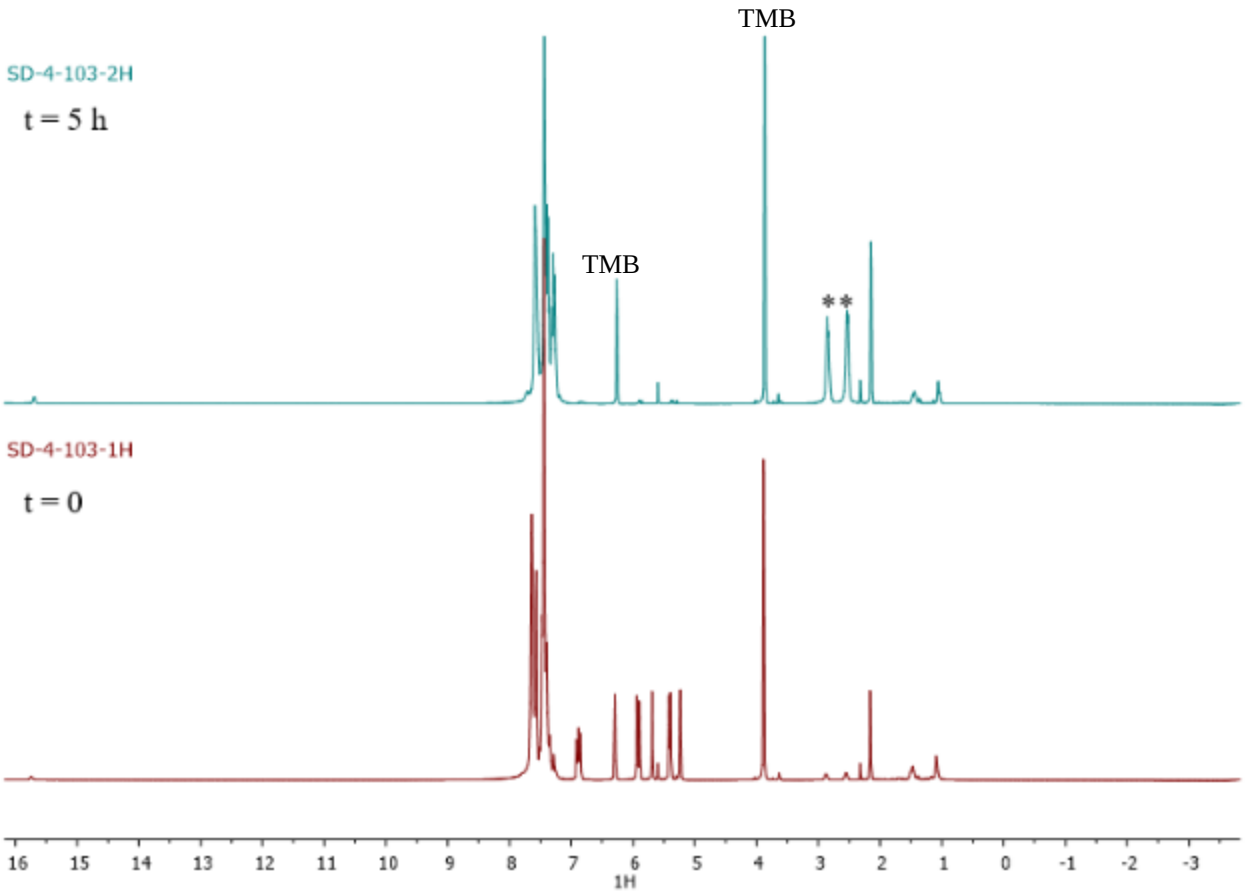
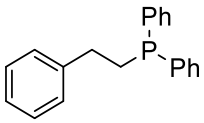


Figure S.17. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of styrene with one equiv. of diphenyl phosphine by 5 mol % of **1** under 360 nm irradiation (continued)

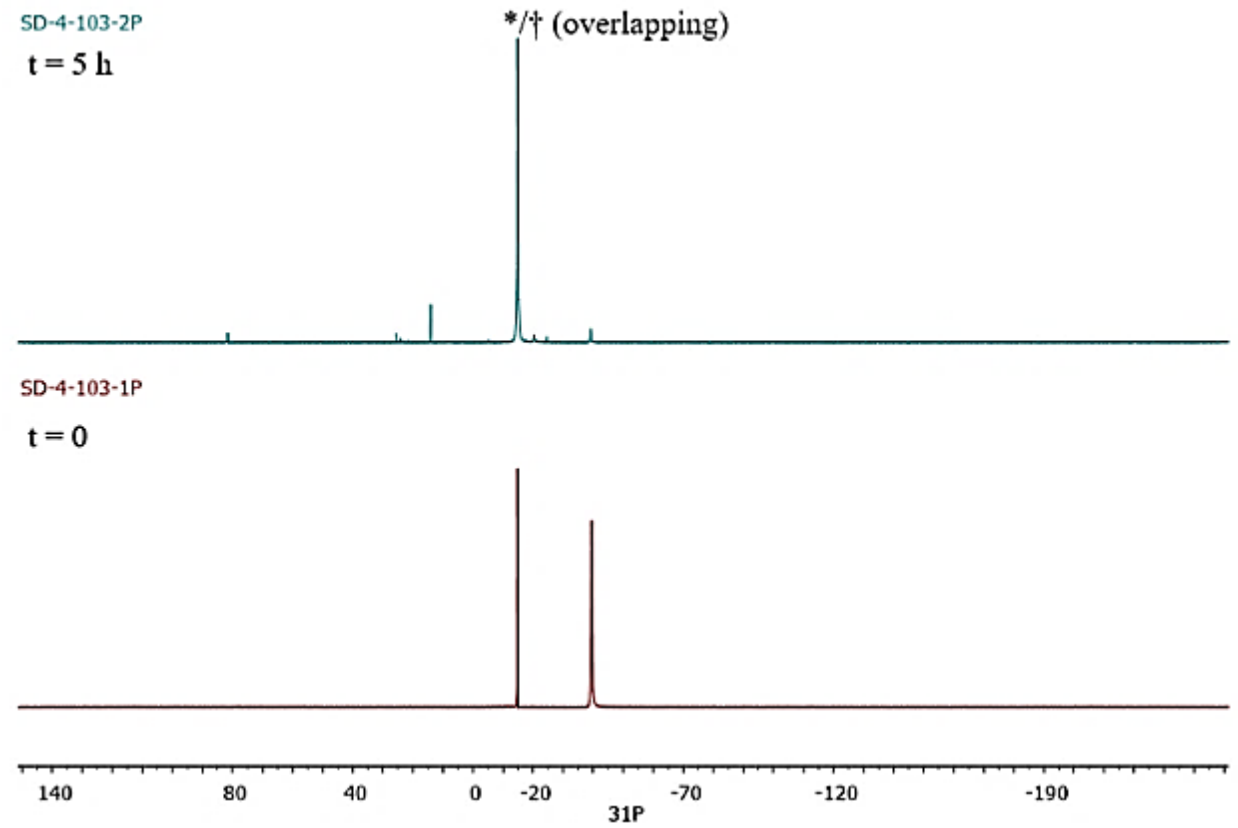
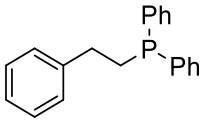


Figure S.18. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of *p*-methylstyrene
Eqn (1)

Prepared in accordance with the general procedure with two equiv. of phenylphosphine**.** After 25 min of 360 nm irradiation, 100% of *p*-methylstyrene was converted with 98:2:6 selectivity for the secondary hydrophosphination product compared to the tertiary product and dehydrocoupled product as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Together, these indicate a 96% conversion of styrene to secondary phosphine. Subsequent trials with an internal standard of 1,3,5-trimethoxybenzene added after 20 min confirm a greater than 90% conversion. Spectra are consistent with previous reports.[6]

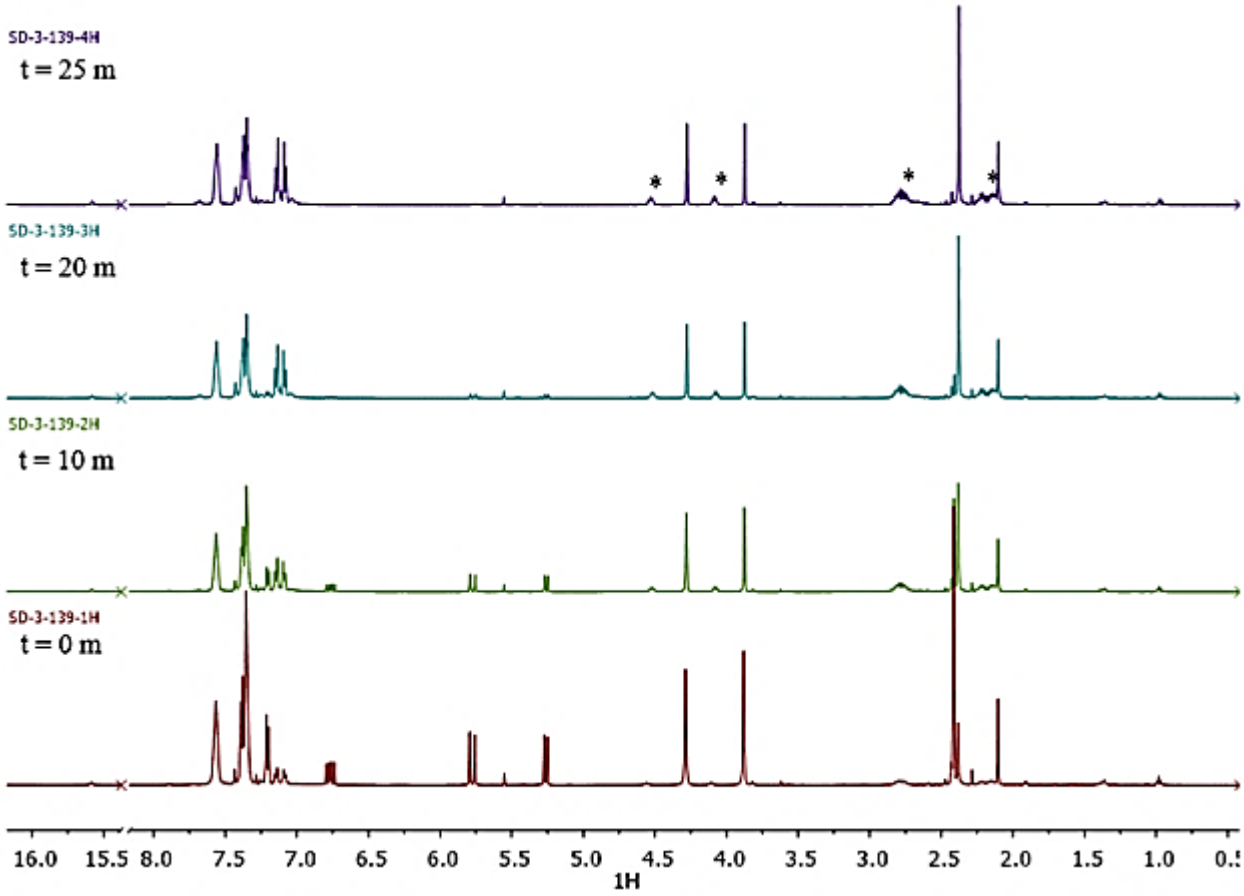
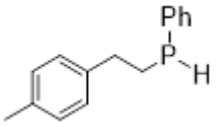


Figure S.19. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of *p*-methylstyrene with two equiv. of phenylphosphine with 5 mol % of **1** under 360 nm irradiation (continued)

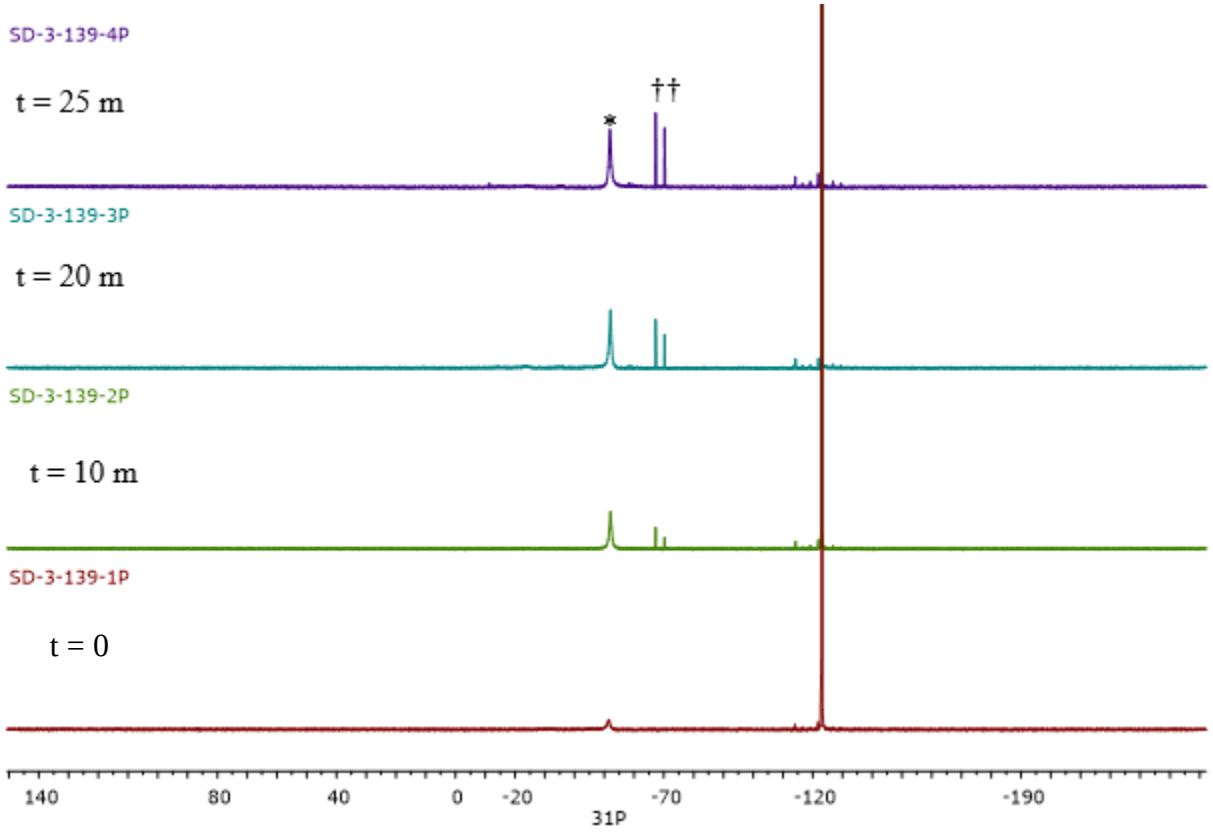
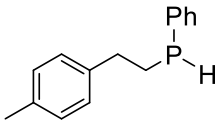


Figure S.20. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of *p*-methylstyrene with one equiv. of diphenylphosphine by **1**
Eqn (2)

Prepared according to the general procedure with one equiv. of diphenylphosphine. 98% conversion of *p*-methylstyrene was observed after 5 h of 360 nm irradiation as measured by ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[21]

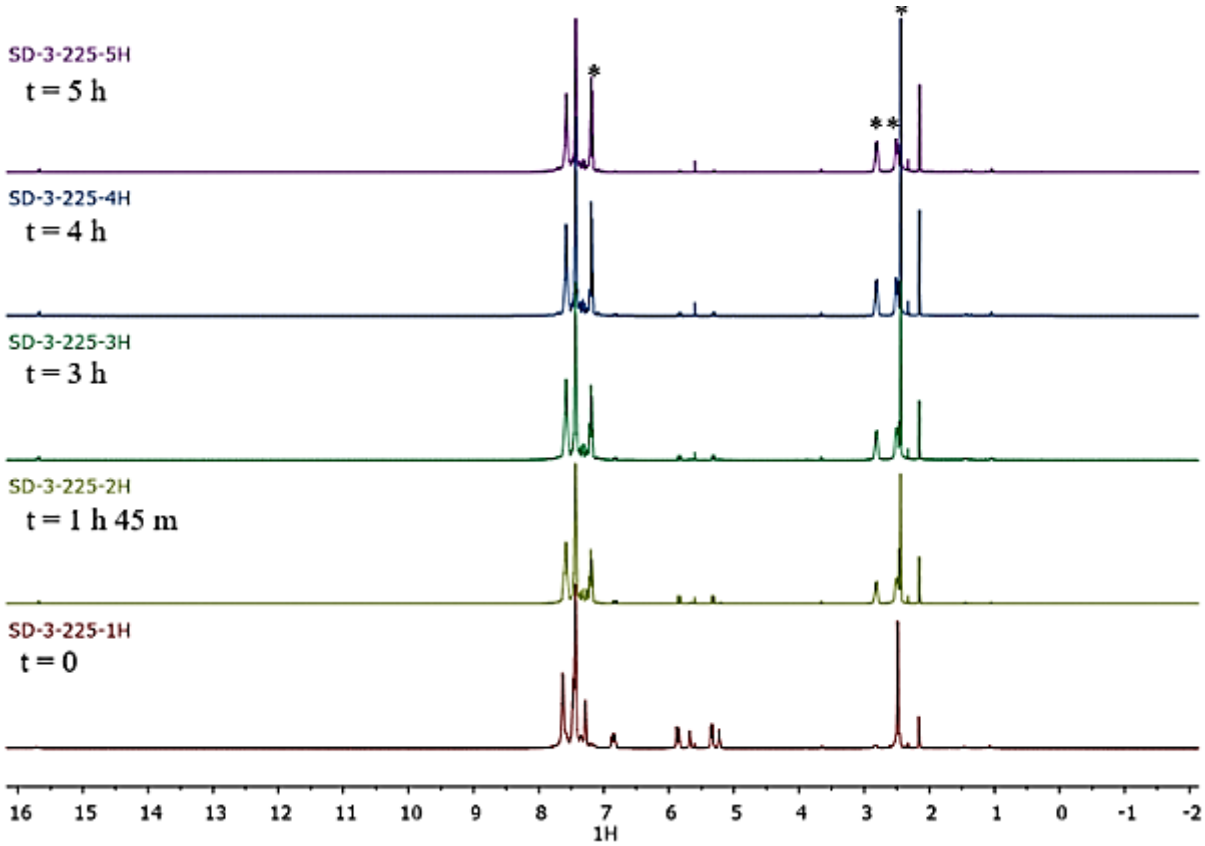
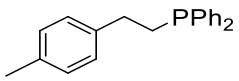


Figure S.21. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of *p*-methylstyrene with one equiv. of diphenylphosphine and 5 mol % of **1** under 360 nm irradiation (continued)

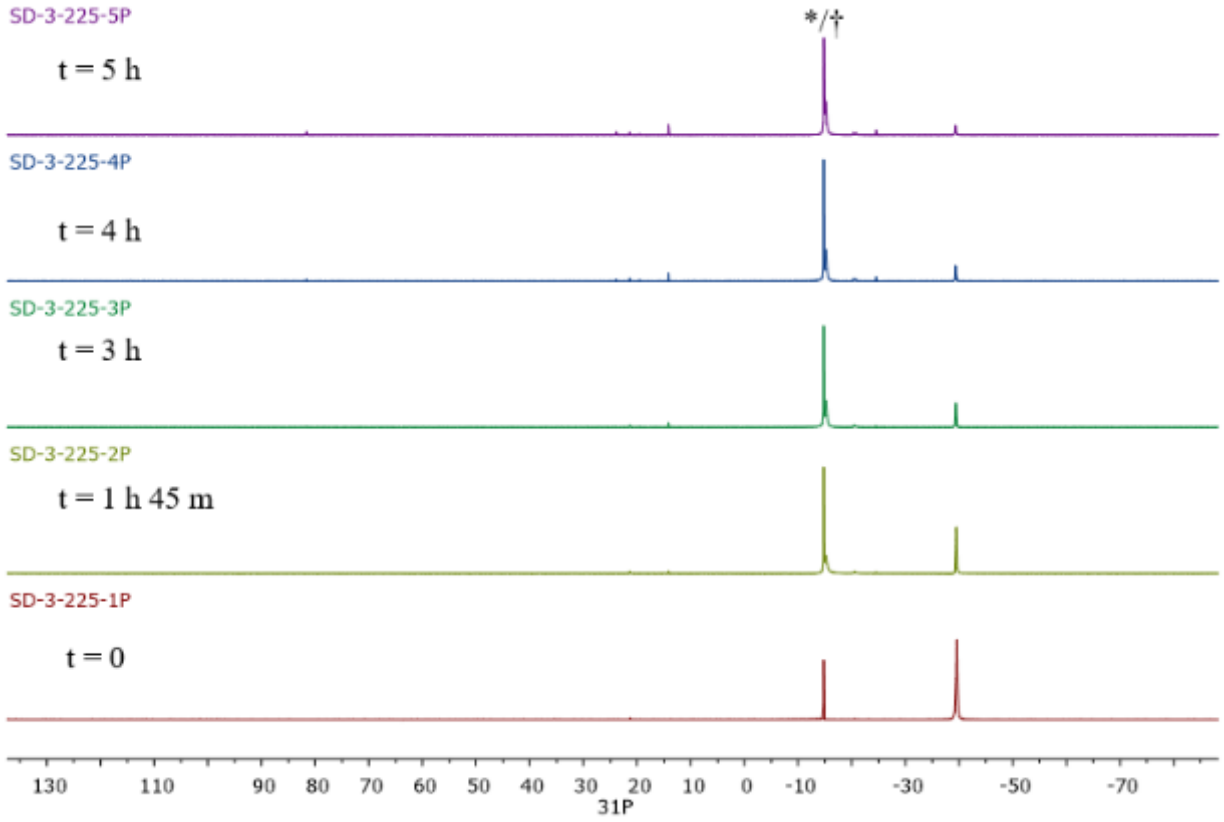
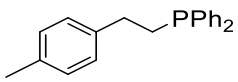


Figure S.22. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of *p*-bromostyrene
Eqn (1)

Prepared in accordance with the general procedure with two equiv. of phenylphosphine. After 20 min of 360 irradiation, 100% of styrene was converted with 97:3:2 selectivity for the secondary hydrophosphination product compared to the tertiary product and dehydrocoupled product as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Together, these indicate a 94% conversion of styrene to secondary phosphine. Spectra are consistent with previous reports.[6]

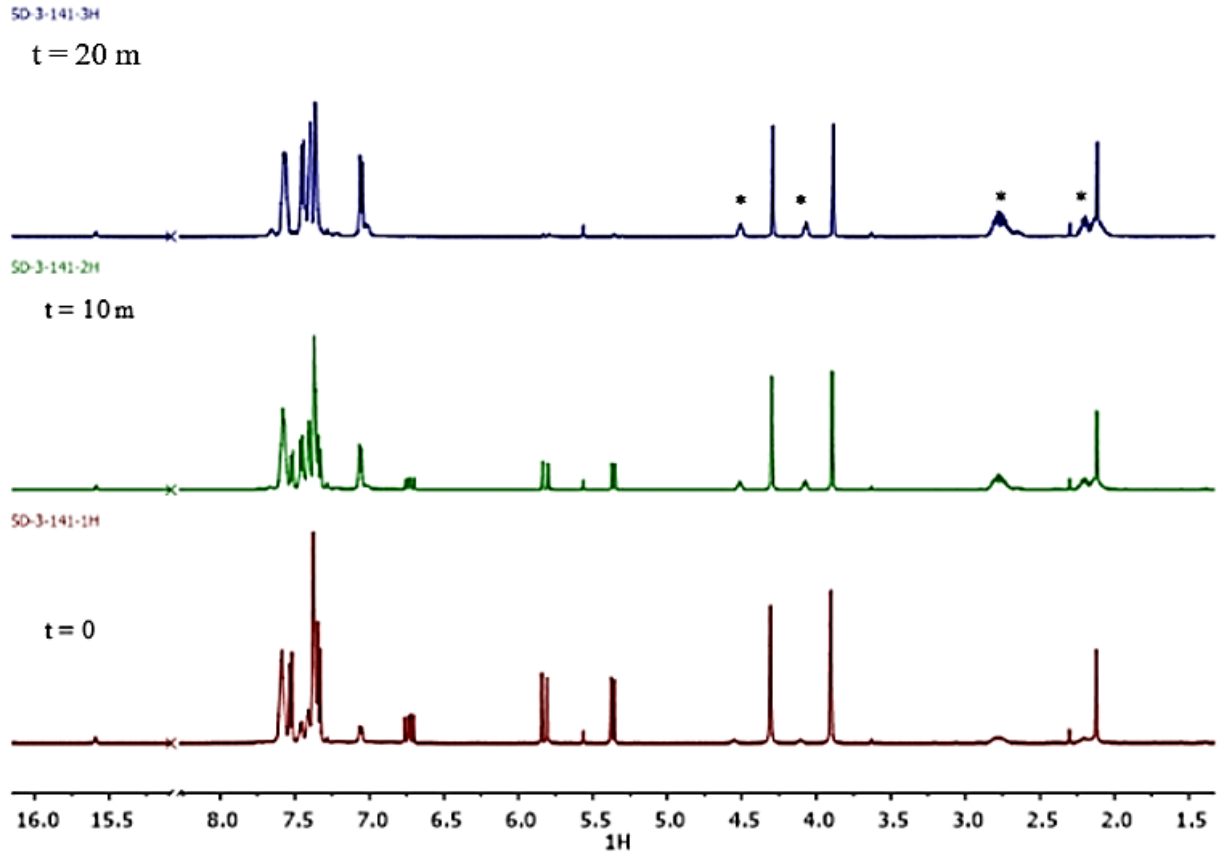
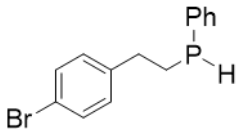


Figure S.23. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of *p*-bromostyrene with two equiv. of phenylphosphine with 5 mol % of **1** under 360 nm irradiation (continued)

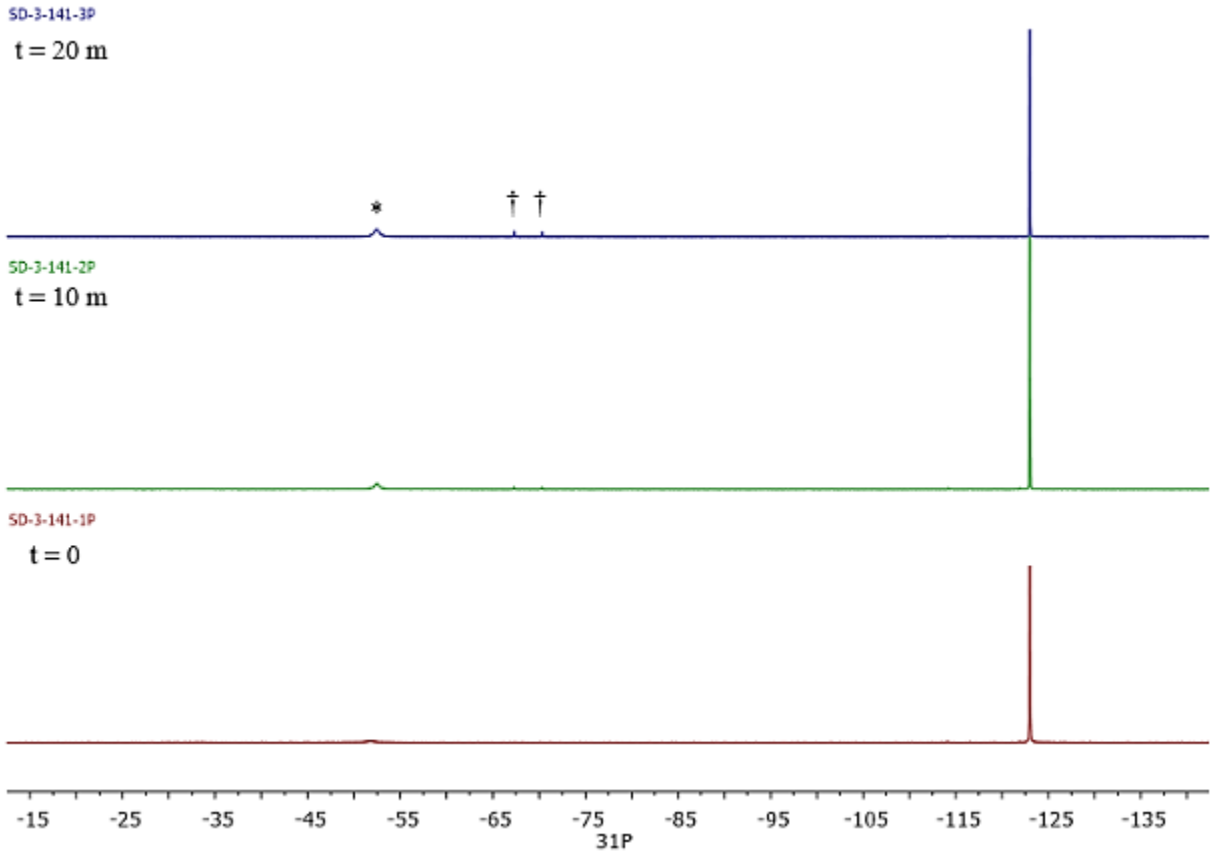
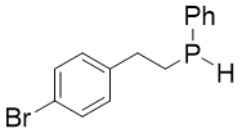


Figure S.24. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of *p*-bromostyrene with one equiv. of diphenylphosphine by **1**
Eqn (2)

Prepared according to general procedure with one equiv. of diphenylphosphine. 88% conversion of *p*-bromostyrene was observed after 5 h and 98% after 8 h as measured by ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[21]

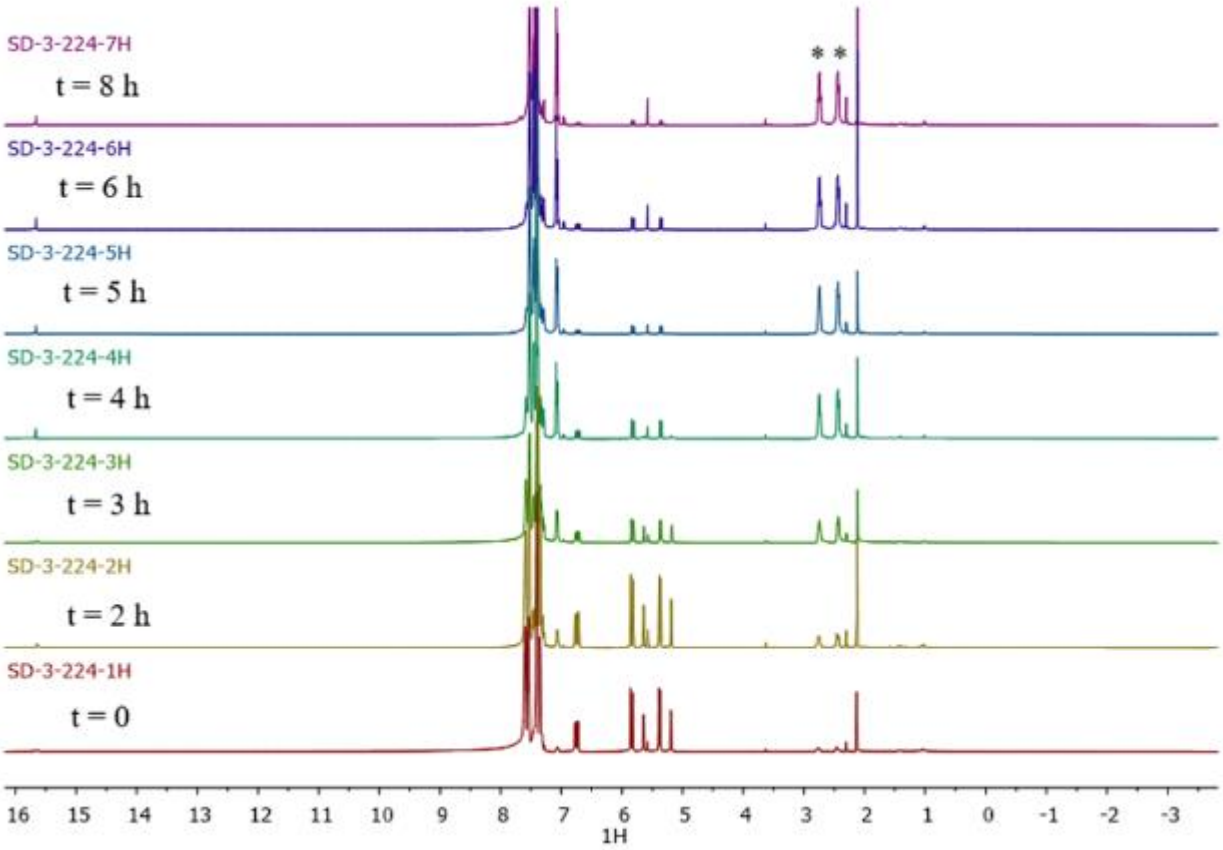
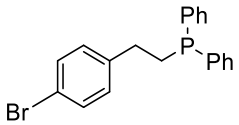


Figure S.25. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of *p*-bromostyrene with one equiv. of diphenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

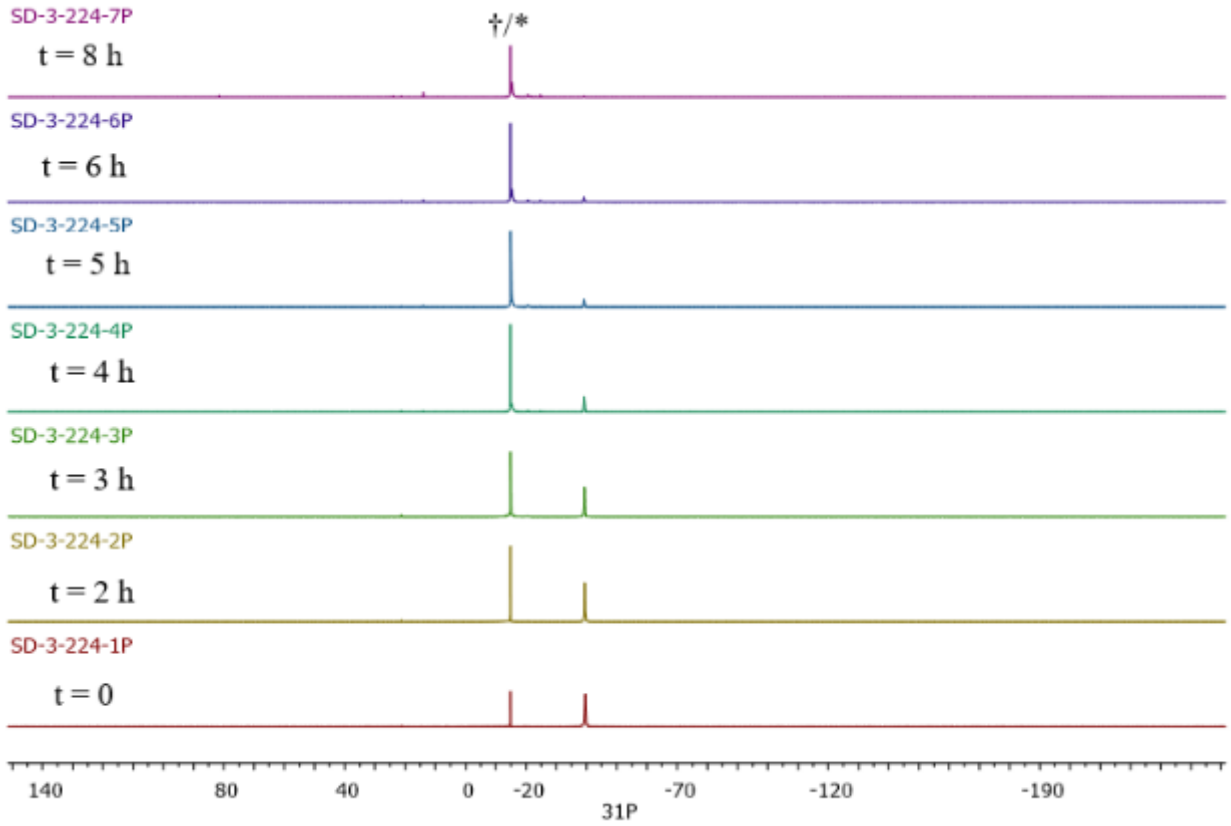
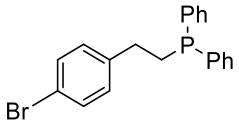


Figure S.26. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-hexene
Eqn (3), and Table 1, **3a**

Prepared by the general procedure. After 7 h of 360 nm irradiation, 72% conversion was measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. After 20 h, 91% of 1-hexene was converted as measured by ^{1}H NMR and 78% was measured by $^{31}P\{^{1}H\}$ NMR spectroscopy. Subsequent reactions measured to an internal standard yielded a similar result. Spectra are consistent with previous reports.[6]

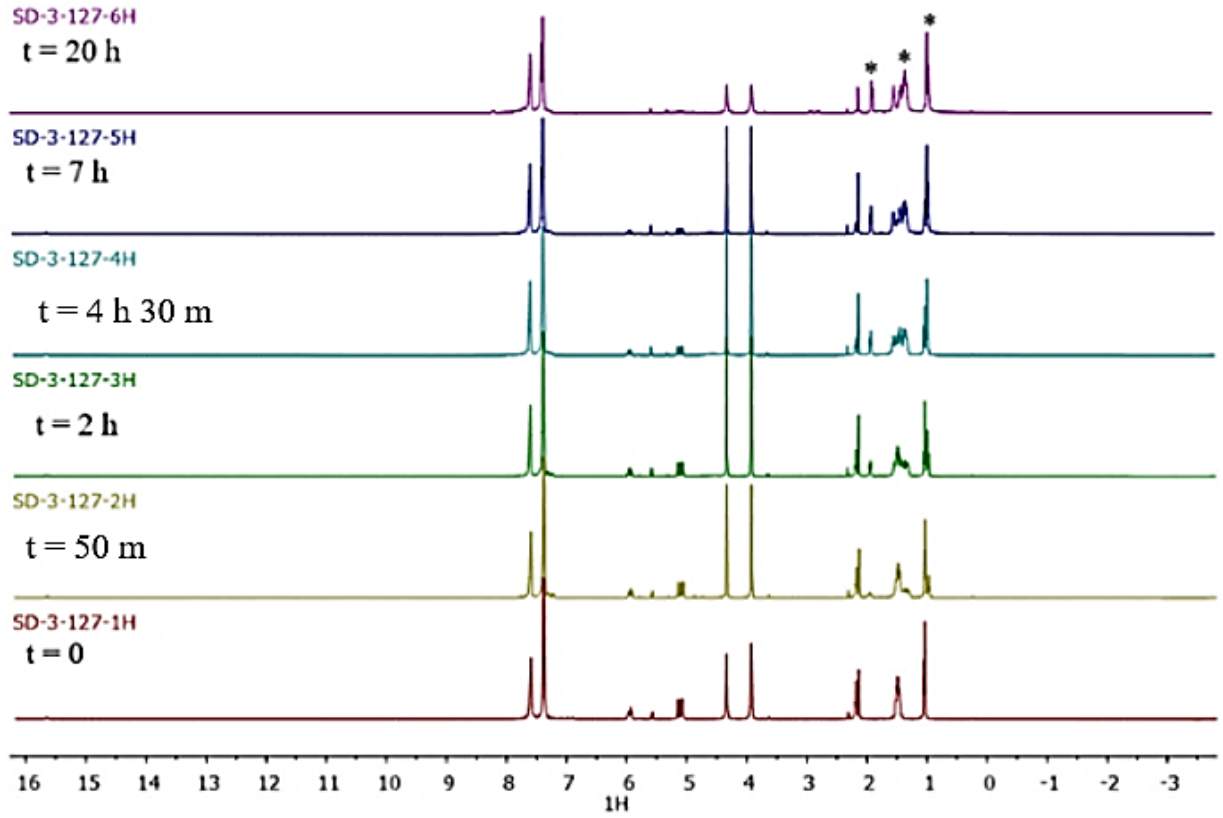
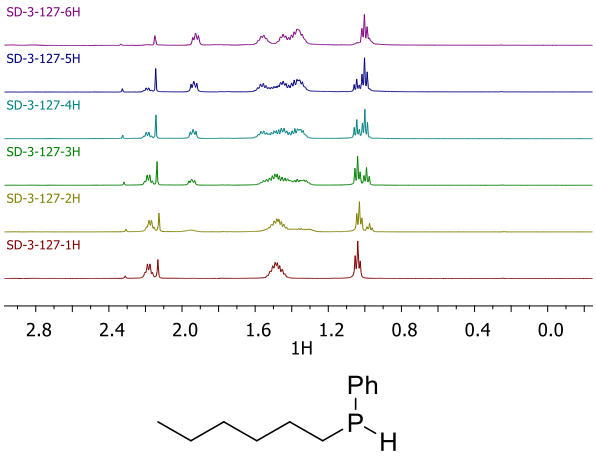


Figure S.27. Stacked ^{1}H NMR spectra ($CDCl_3$ 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-hexene with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

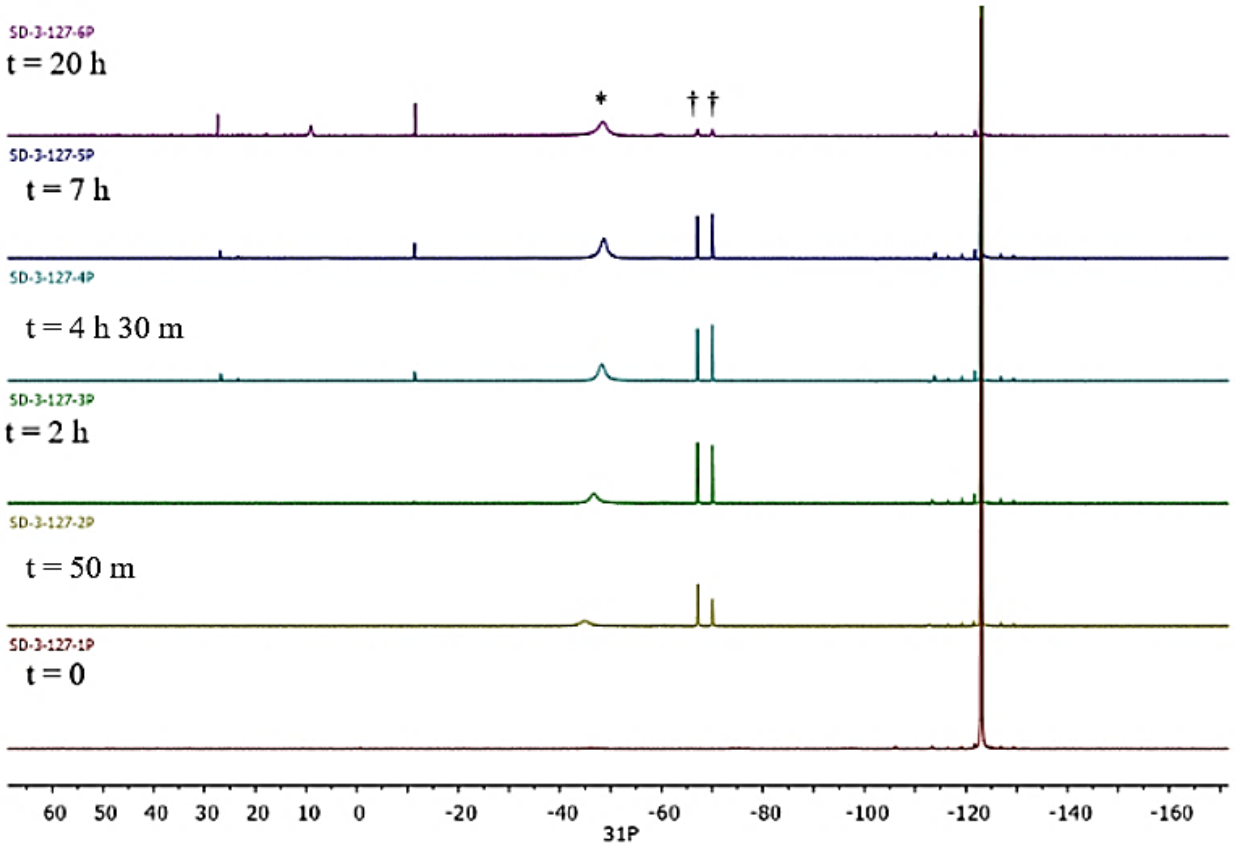
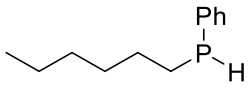


Figure S.28. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-hexene with three equiv. of diphenylphosphine by **1** – neat
Table 1, **3b**

In an N_2 filled dry box, 2.28 mmol (424.2 mg, 396 µL) of diphenylphosphine, 0.76 mmol of 1-hexene and 0.038 mmol (10 mg) of **1** were measured and mixed in a J-Young type polytetrafluoroethylene-valved NMR tube. Initial ^{13}C and $^{31}P\{^1H\}$ NMR spectra were then obtained. After the initial NMR spectra, the reaction was irradiated for 24 h under 360 nm irradiation. A second ^{13}C and $^{31}P\{^1H\}$ NMR spectra were then obtained. Then a ^1H NMR spectra was obtained after adding 200 µL $CDCl_3$ mixed with 16.3 mg (0.097 mmol) 1,3,5-trimethoxybenzene as an internal standard. 100% conversion of 1-hexene occurred as measured by ^1H NMR spectroscopy. Ingratiation of the crude ^1H NMR spectra to the internal standard results in between 64 -74% conversion depending on peak integrated and agrees with integration of the $^{31}P\{^1H\}$ NMR spectra. The catalyst was then removed by silica gel chromatography with 3:1 Hexanes DCM liquid phase in order to get cleaner integrations.

Note: This trial was scaled up in order to obtain spectra ^{31}P NMR spectra of the reaction without addition of solvent and to allow for cleaner integrations after removal of catalyst. Comparable results were achieved under the standard conditions.

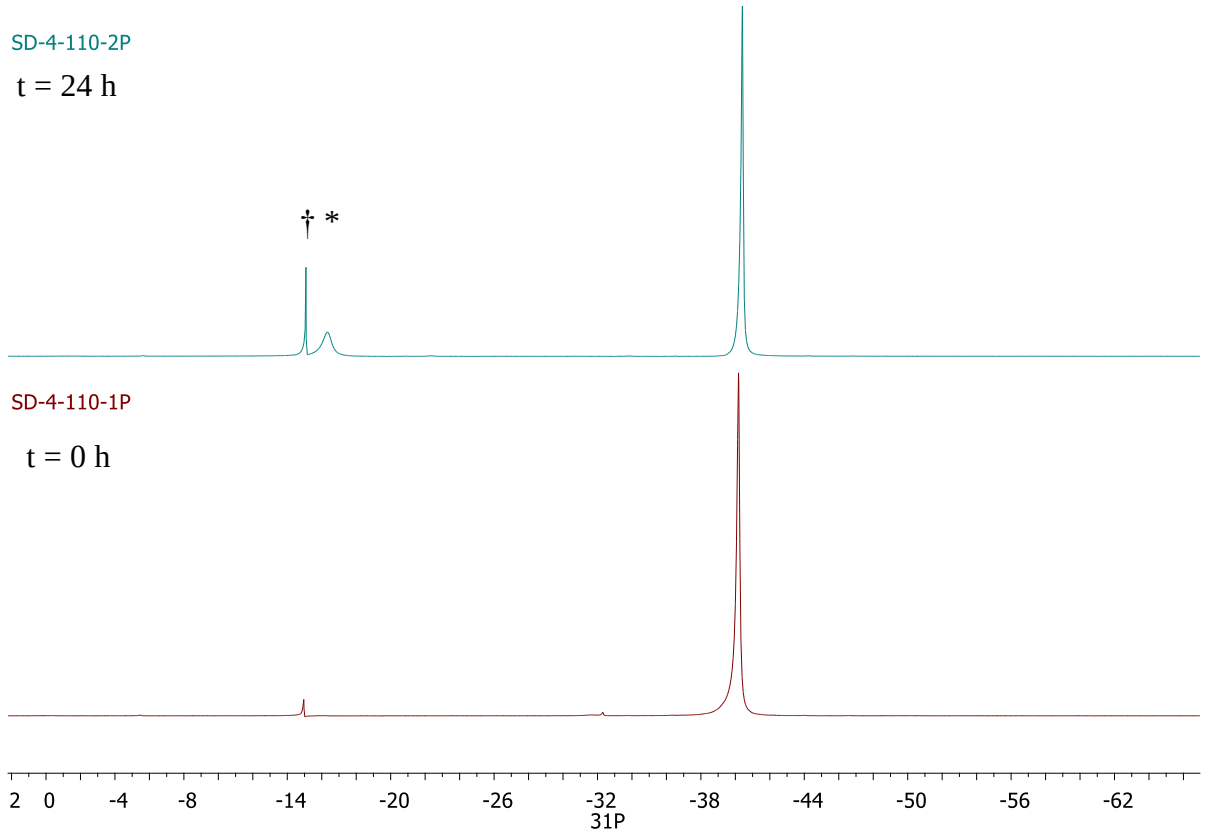
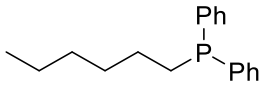


Figure S.29. Stacked $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-hexene with three equiv. of diphenylphosphine by **1** – neat (continued)

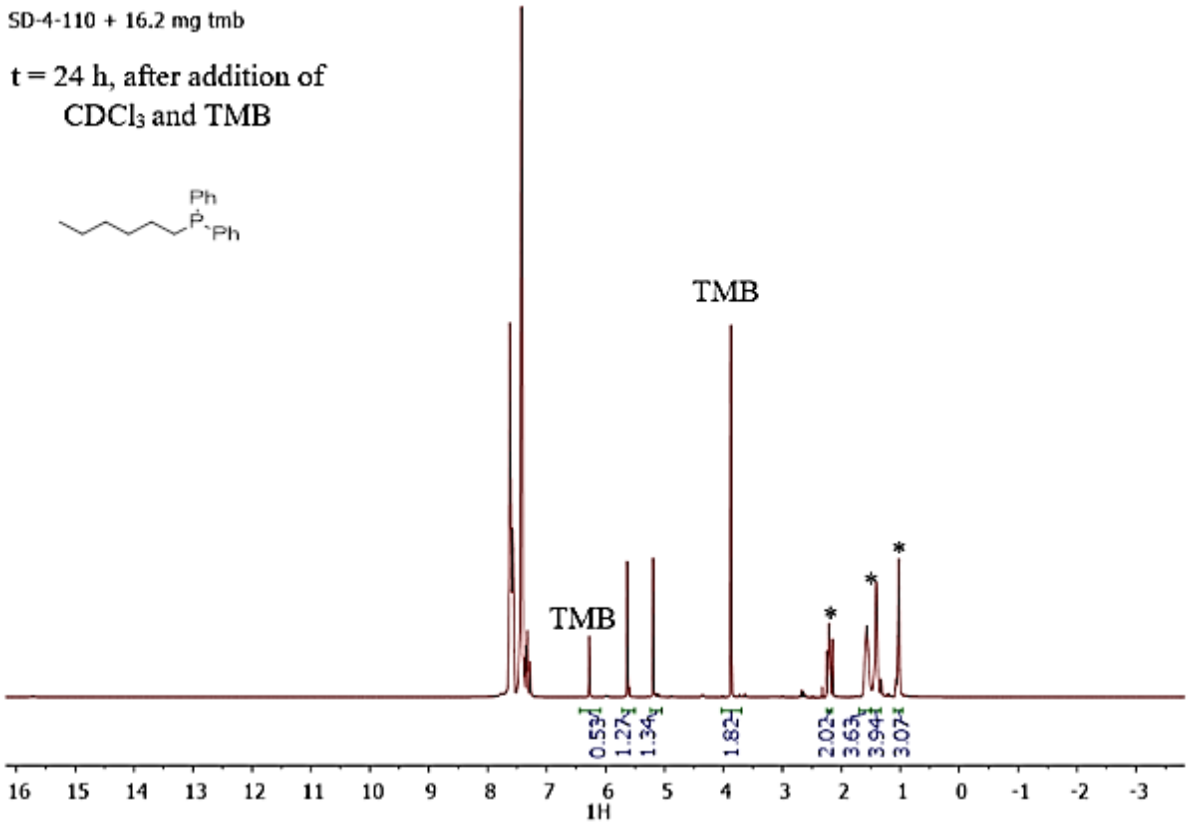


Figure S.30. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) at 24 h of 360 nm irradiation after addition of 1,3,5-trimethoxybenzene**.**

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-hexene with three equiv. of diphenylphosphine by **1** – neat (continued)

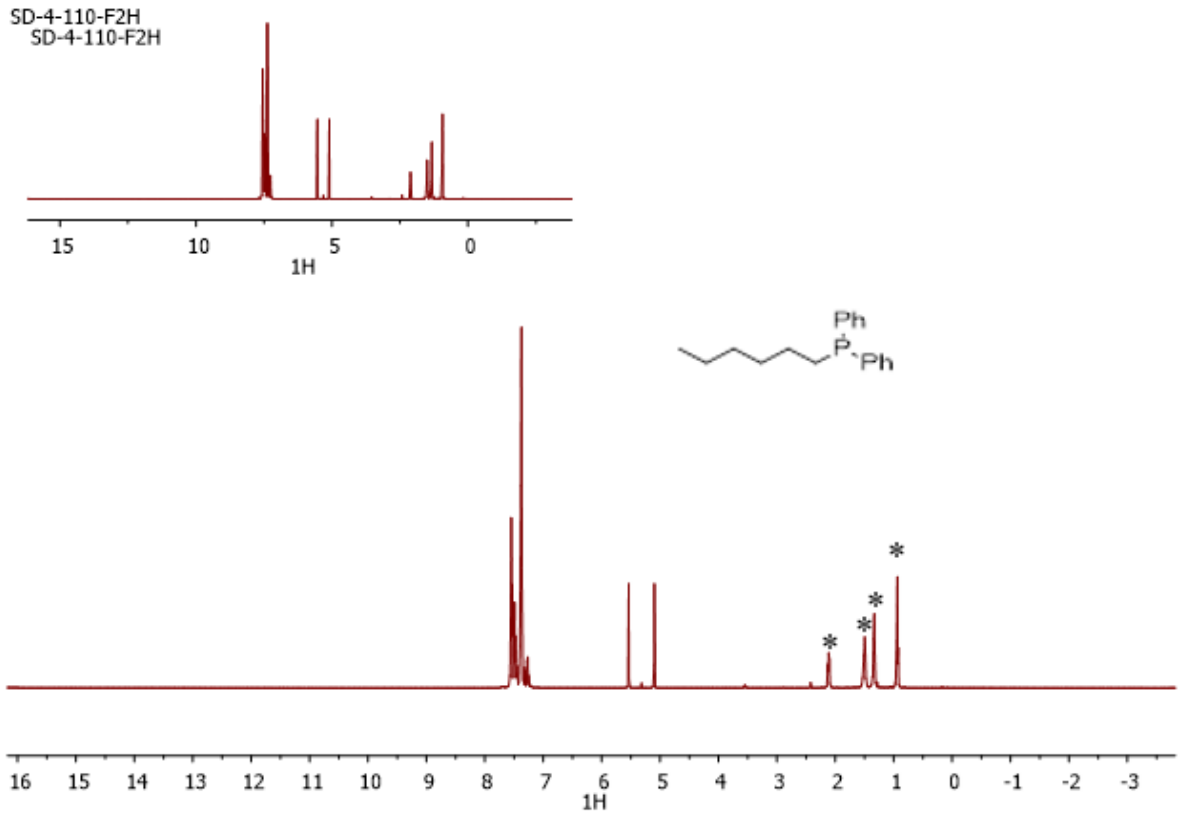


Figure S.31. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of a fraction with **1** removed

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-hexene with three equiv. of diphenylphosphine by **1** – neat – (continued)

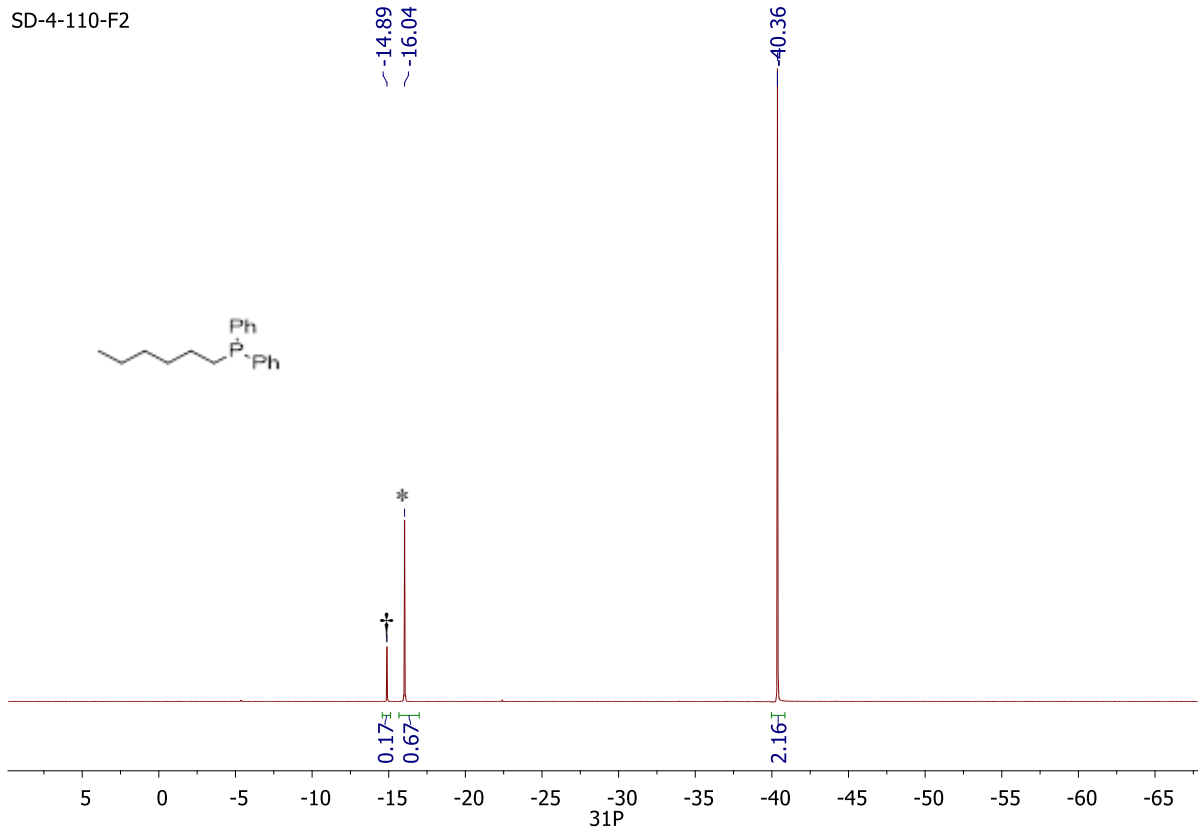


Figure S.32. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 202 MHz) of a fraction with **1** removed

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Attempted hydrophosphination of 1-hexene with one equiv. of diphenylphosphine by **1** in $CDCl_3$

Prepared according to the general procedure with one equiv. of diphenylphosphine and 9.8 mg of 1,3,5-trimethoxybenzene as an internal standard. 25% conversion of diphenylphosphine to a mixture of products was measured by $^{31}P\{^1H\}$ NMR spectroscopy after 24 h of 360 nm irradiation. New alkyl peaks corresponding to 14% conversion were observed in the ^1H NMR spectra. However, we were unable to unambiguously characterize this as the anti-markovnikov hydrophosphination product due to overlapping peaks and thus is not reported.

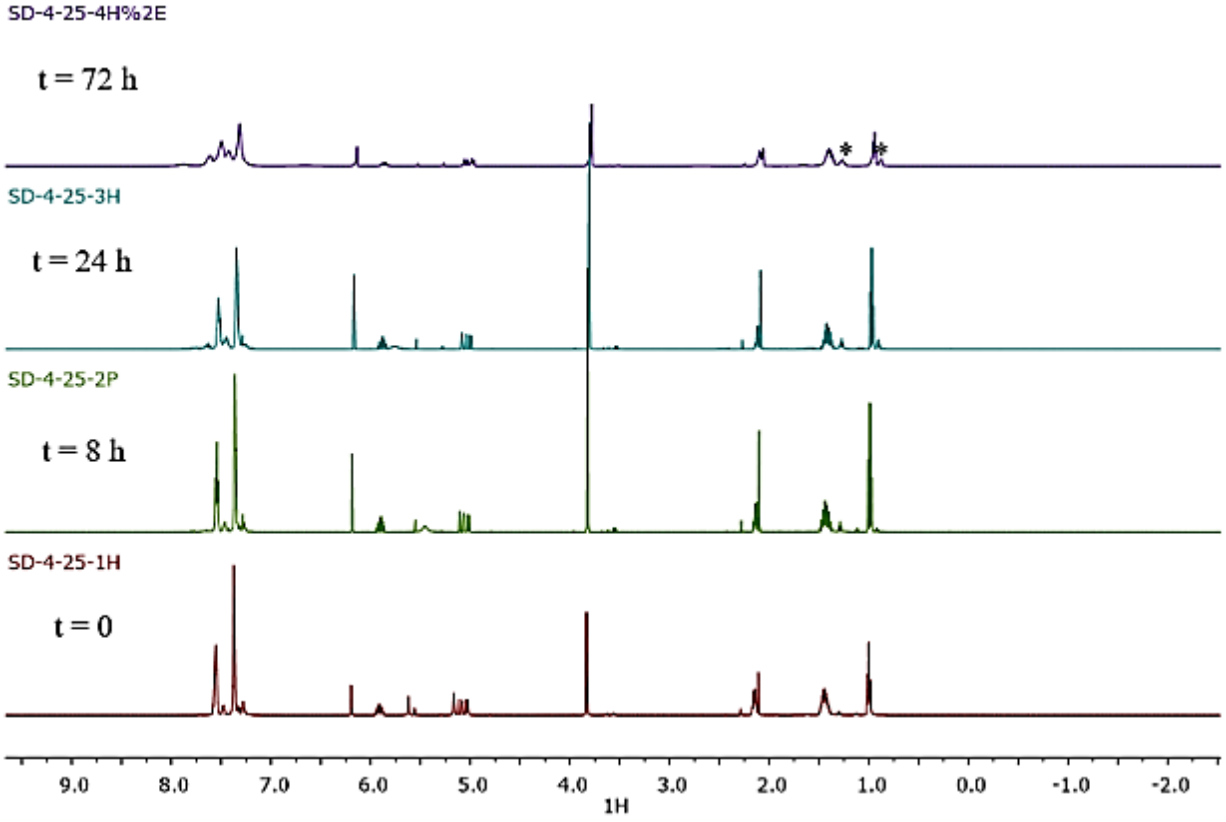


Figure S.33. Stacked ^1H NMR spectra ($CDCl_3$, 500 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Attempted hydrophosphination of 1-hexene with one equiv. of diphenylphosphine by **1** in $CDCl_3$ (continued)

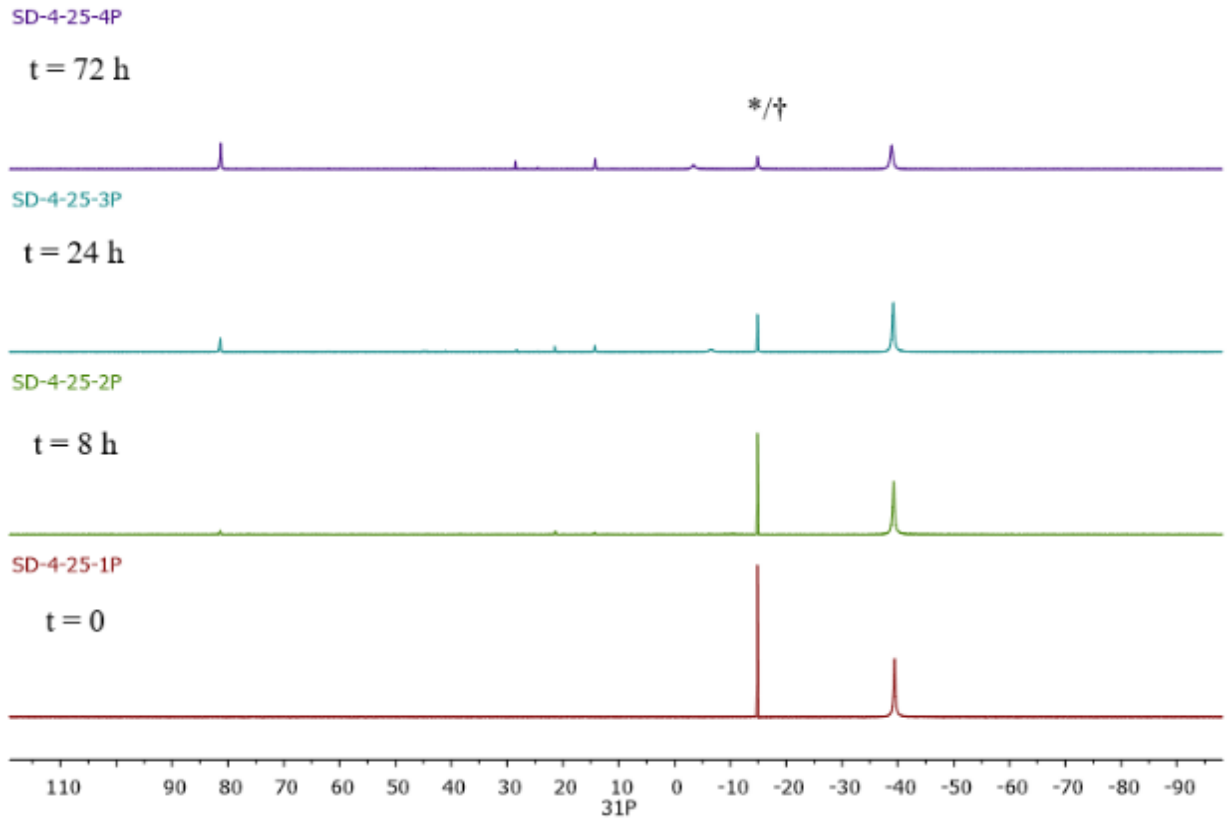


Figure S.34. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-heptene
Table 1, **3c**

Prepared by the general procedure. After 16 h of 360 nm irradiation, 73% conversion was measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[6]

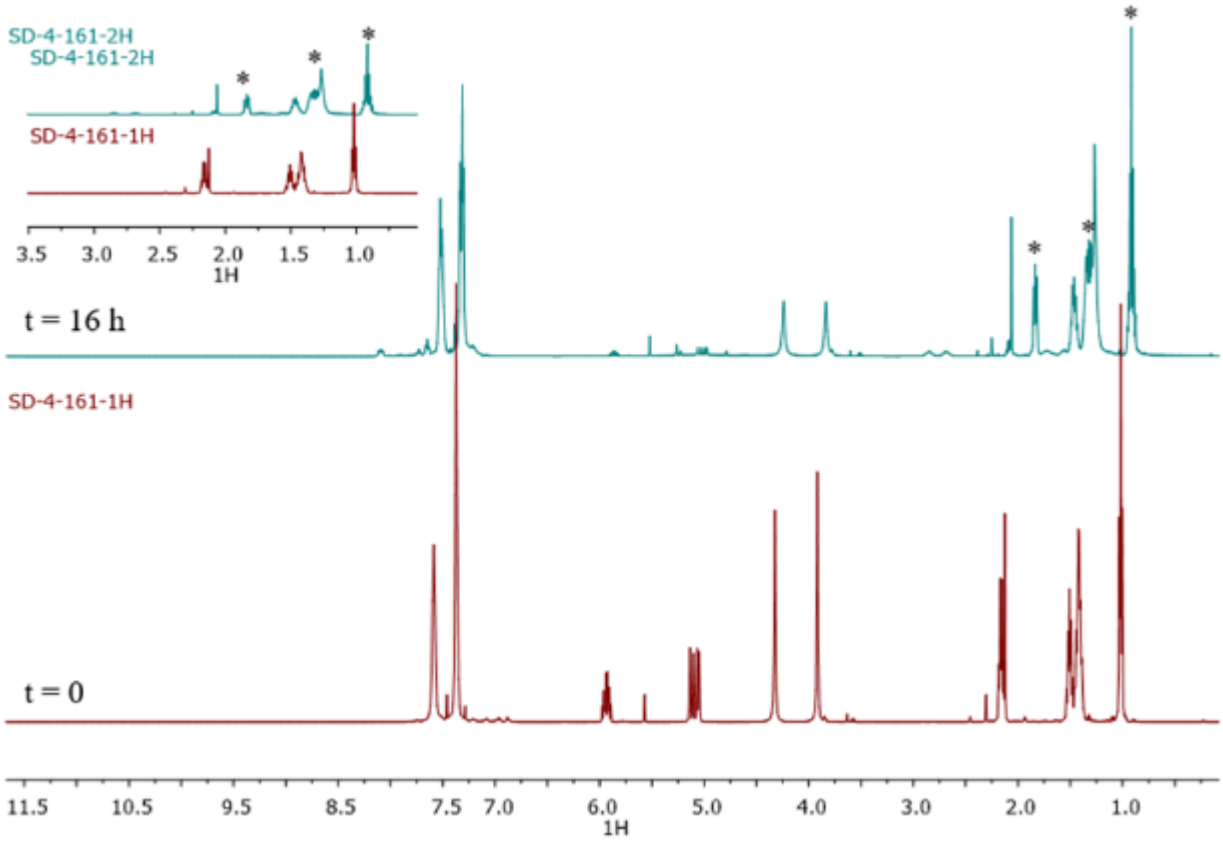
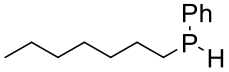


Figure S.35. Stacked ^{1}H NMR spectra ($CDCl_3$ 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-heptene with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

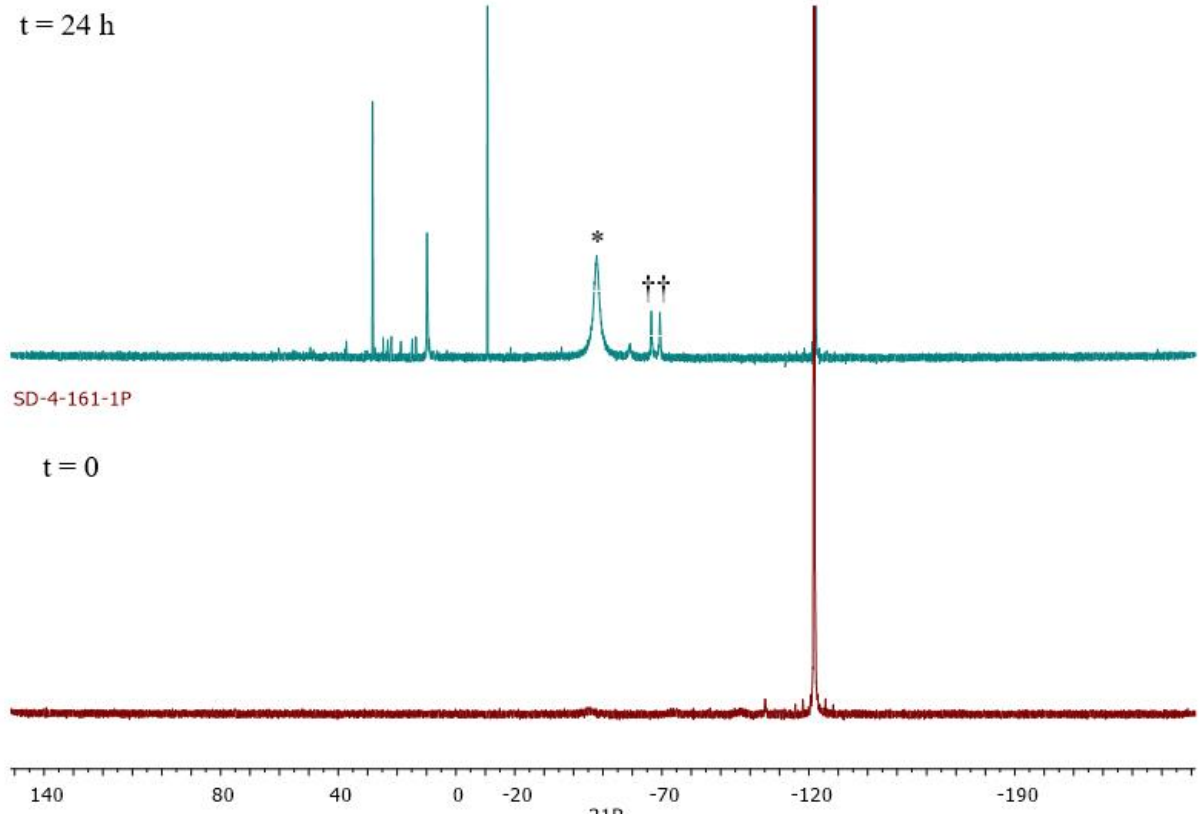
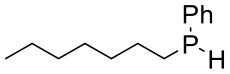


Figure S.36. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-octene
Table 1, **3d**

Prepared according to the general procedure with two equiv. of phenylphosphine. 88% conversion of 1–octene was observed after 16 h of 360 nm irradiation as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[6]

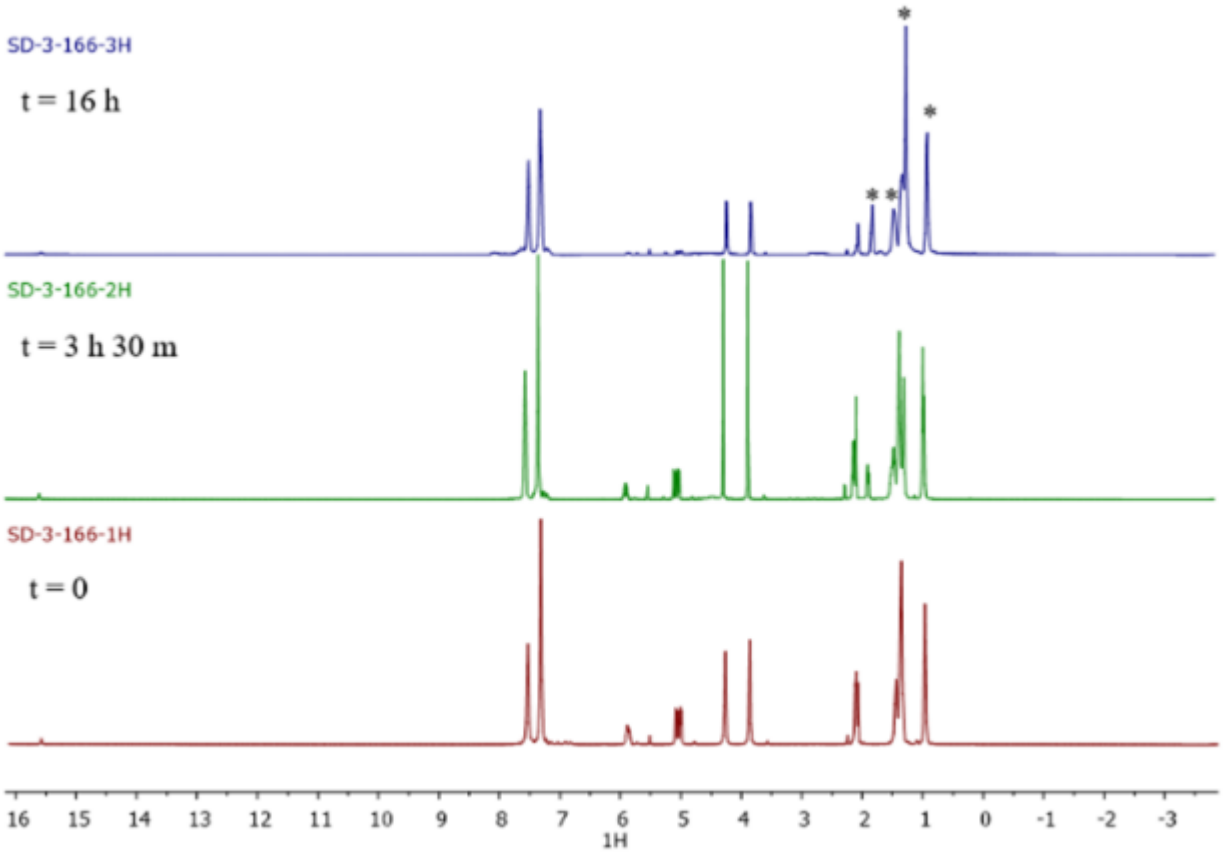
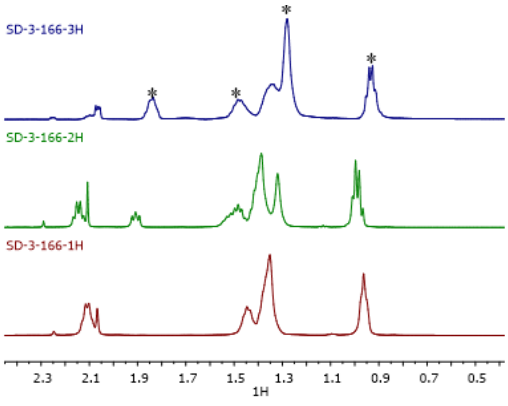
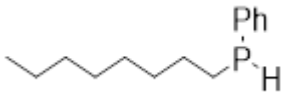


Figure S.37. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)





* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1–octene with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

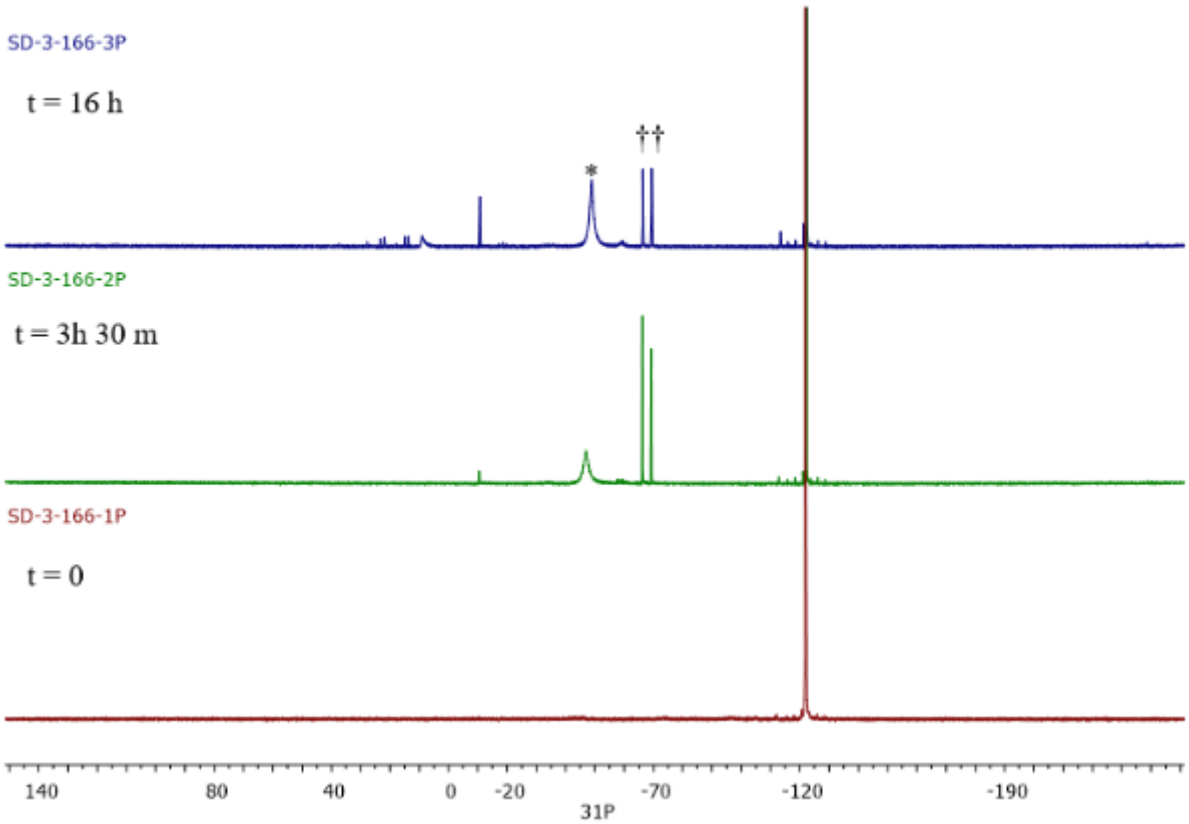
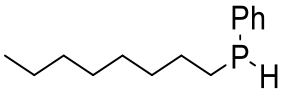


Figure S.38. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of ethoxy ethene
Table 1, **3e**

Prepared according to the general procedure with two equiv. of phenylphosphine. In an N_2 filled dry box, 0.76 mmol of phenylphosphine (83.5µL, 83.5 mg) and 0.38 mmol of ethoxy ethene (27.4 mg) were mixed in 0.5 mL $CDCl_3$. This solution was then pipetted into a 4 ml shell vial containing 5 mg (0.0019 mmol) **1** in 100 µL $CDCl_3$. The resulting yellow solution was quickly transferred to an NMR tube, capped with a disposable NMR cap, and parafilm was wrapped around the NMR cap and shielded from ambient light. After initial ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were obtained, the reaction was irradiated with 360 nm light and monitored periodically. The yellow solution faded over time to clear. After 8 h of 360 nm irradiation, 100% of ethoxy ethene was converted. Integration of the ^{1}H and $^{31}P\{^{1}H\}$ NMR signals indicated an 84% conversion of ethoxy ethene to secondary phosphine. Replication of this reaction indicated that the reaction went to completion in 6 h. Spectra are consistent with previous literature reports.[5]

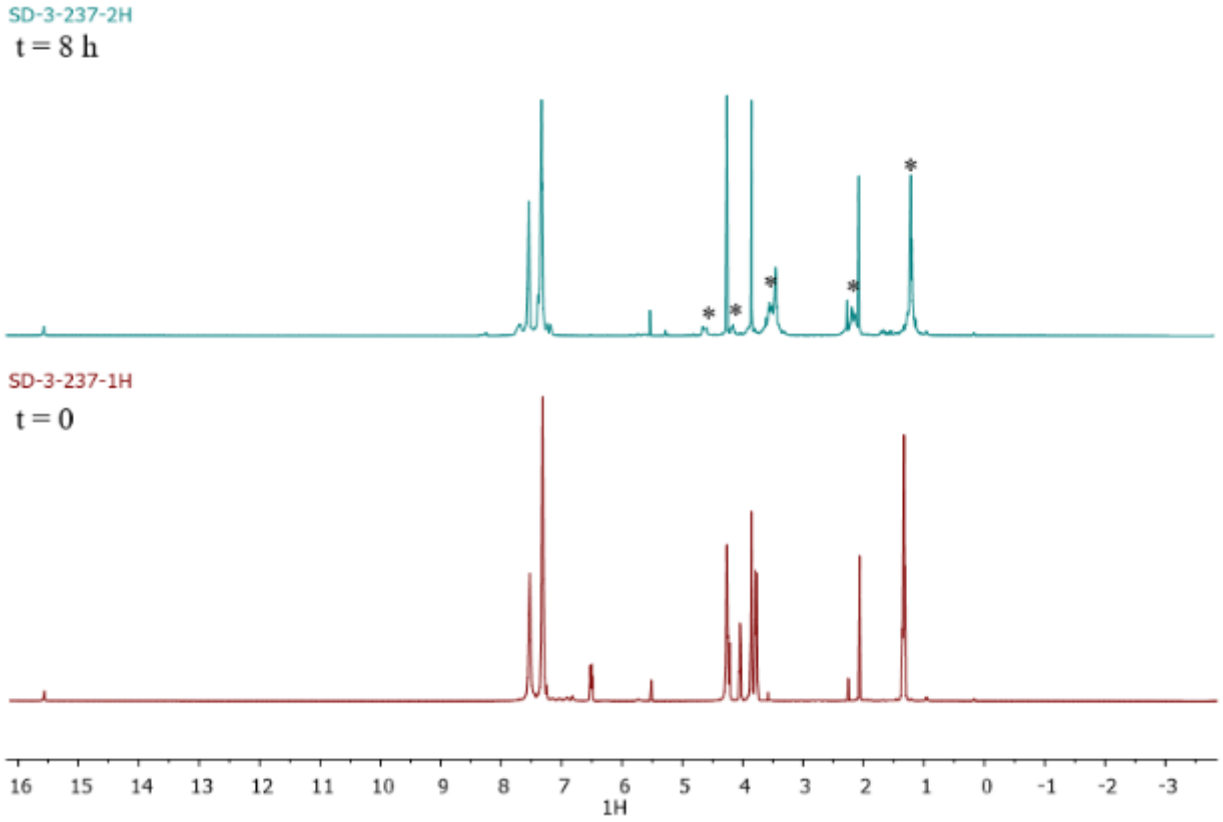
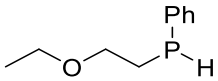


Figure S.39. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of ethoxy ethene with phenylphosphine with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

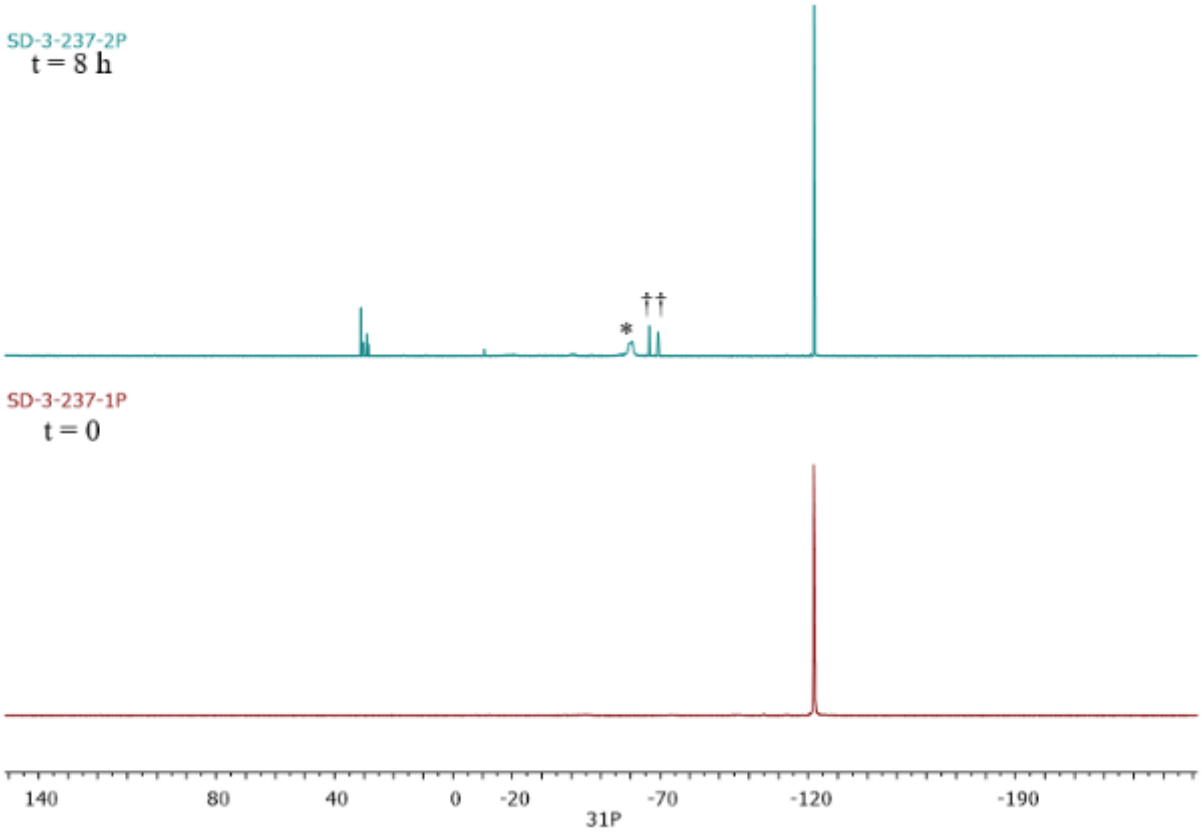
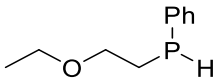


Figure S.40. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of ethoxy ethene with three equiv. of diphenylphosphine by **1** – neat
Table 1, **3f**

Prepared according to the general procedure with the following modifications: 1) no solvent was used 2) three equiv. of diphenylphosphine was used 3) no initial ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra was obtained 4) After 24 h, 5 mg 1,3,5 trimethoxy-benzene was added and 0.5 ml of $CDCl_3$ was added to the NMR tube and ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were obtained. 55% conversion to the hydrophosphination product was measured by integration to the internal standard and ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra is in accordance with the previous reports.[21]

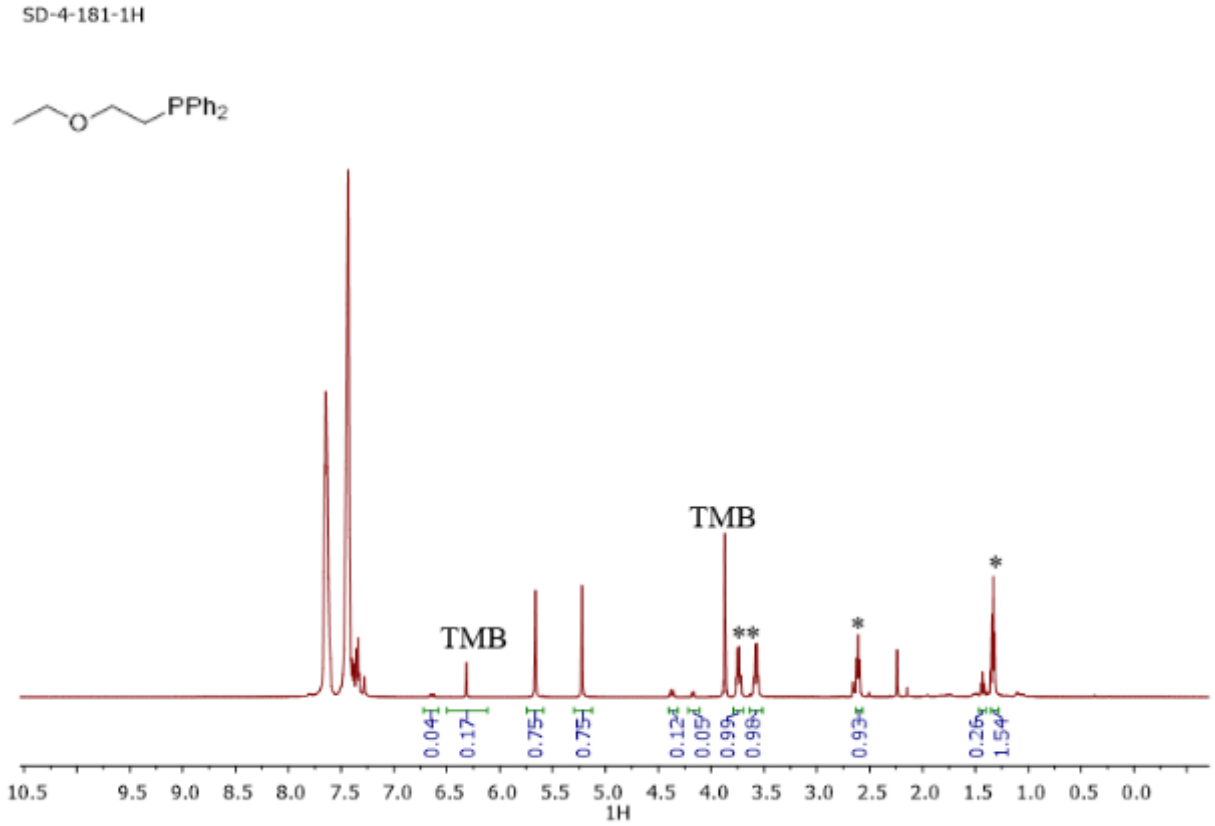


Figure S.41. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) at 24 h of 360 nm irradiation

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of ethoxy ethene with three equiv. of diphenylphosphine by 5 mol % of **1** – neat (continued)

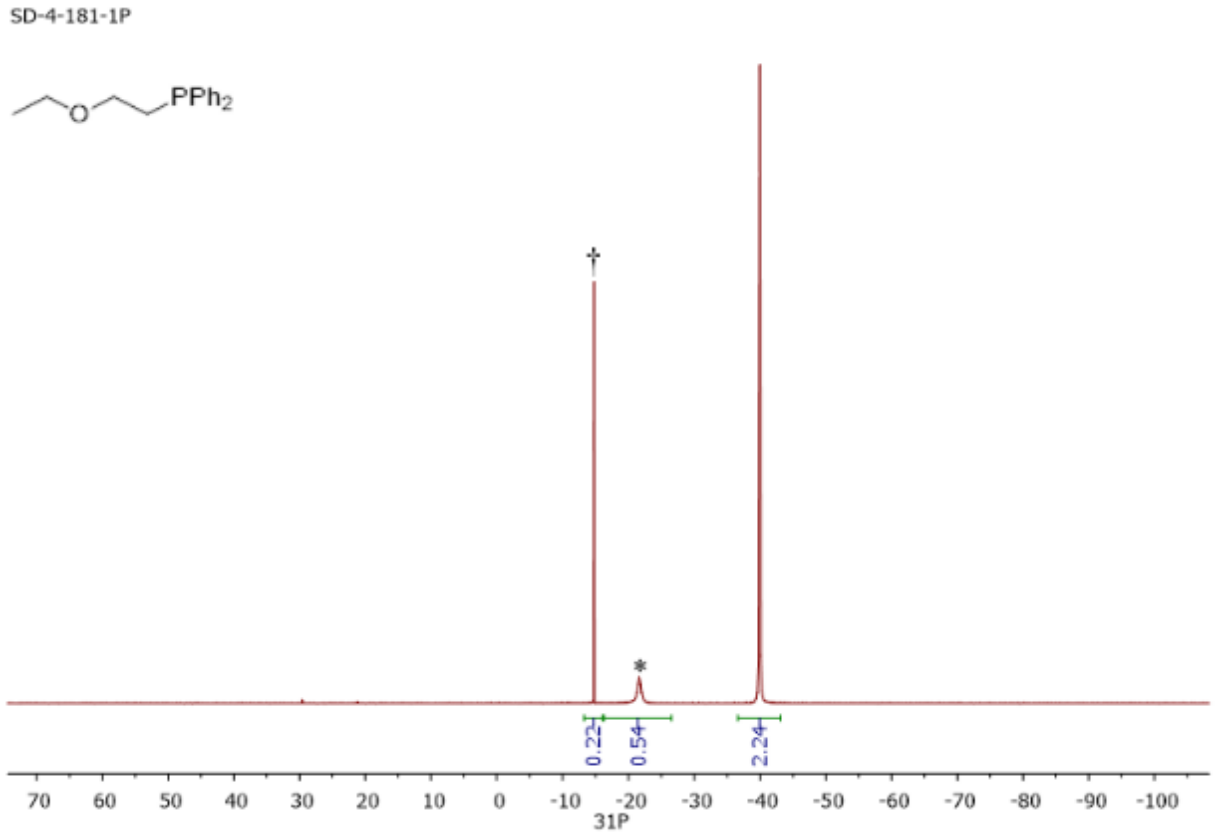


Figure S.42. $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz) at 24 h of 360 nm irradiation

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of allyl benzene
Table 1, **3g**

Prepared by the general procedure with two equiv. of phenylphosphine. 74% conversion of allyl benzene was observed after 16 h of 360 nm irradiation as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[6]

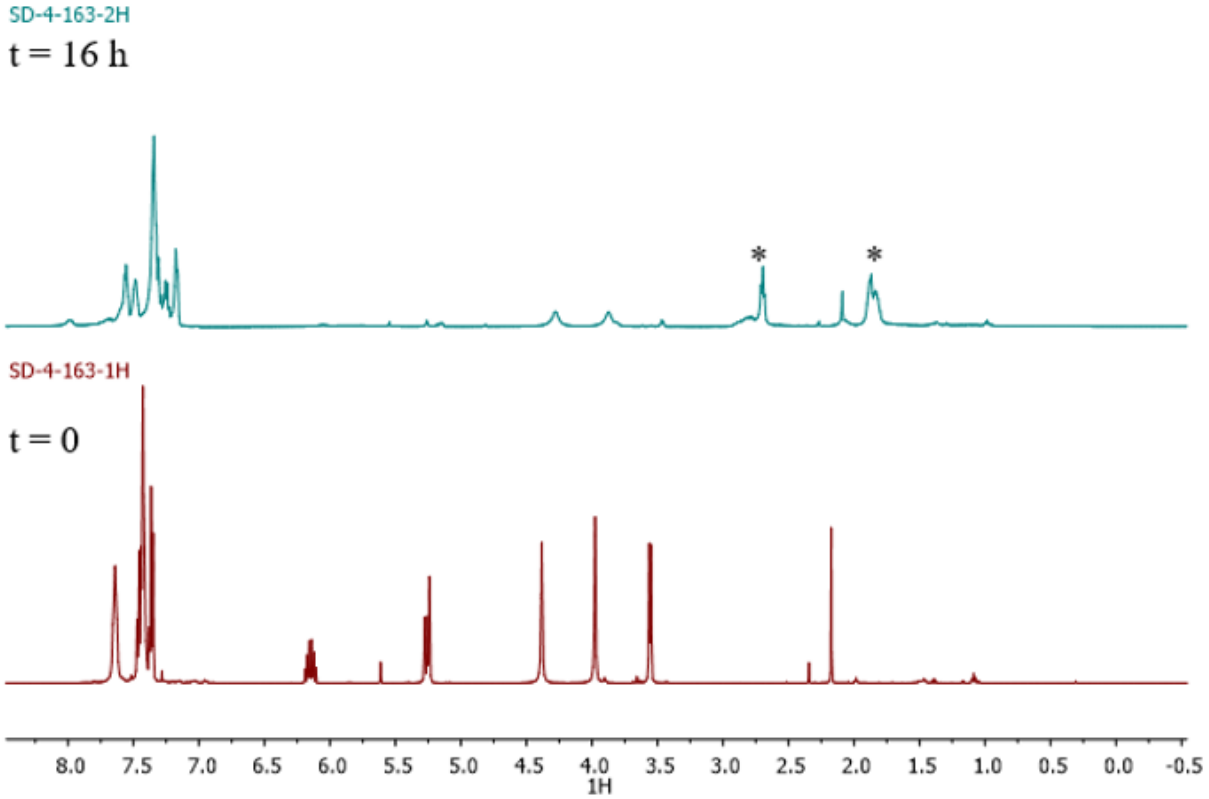
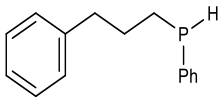


Figure S.43. Stacked ^{1}H NMR spectra ($CDCl_3$ 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of allyl benzene with two equiv. of phenyphosphine and 5 mol % of **1** under 360 nm irradiation

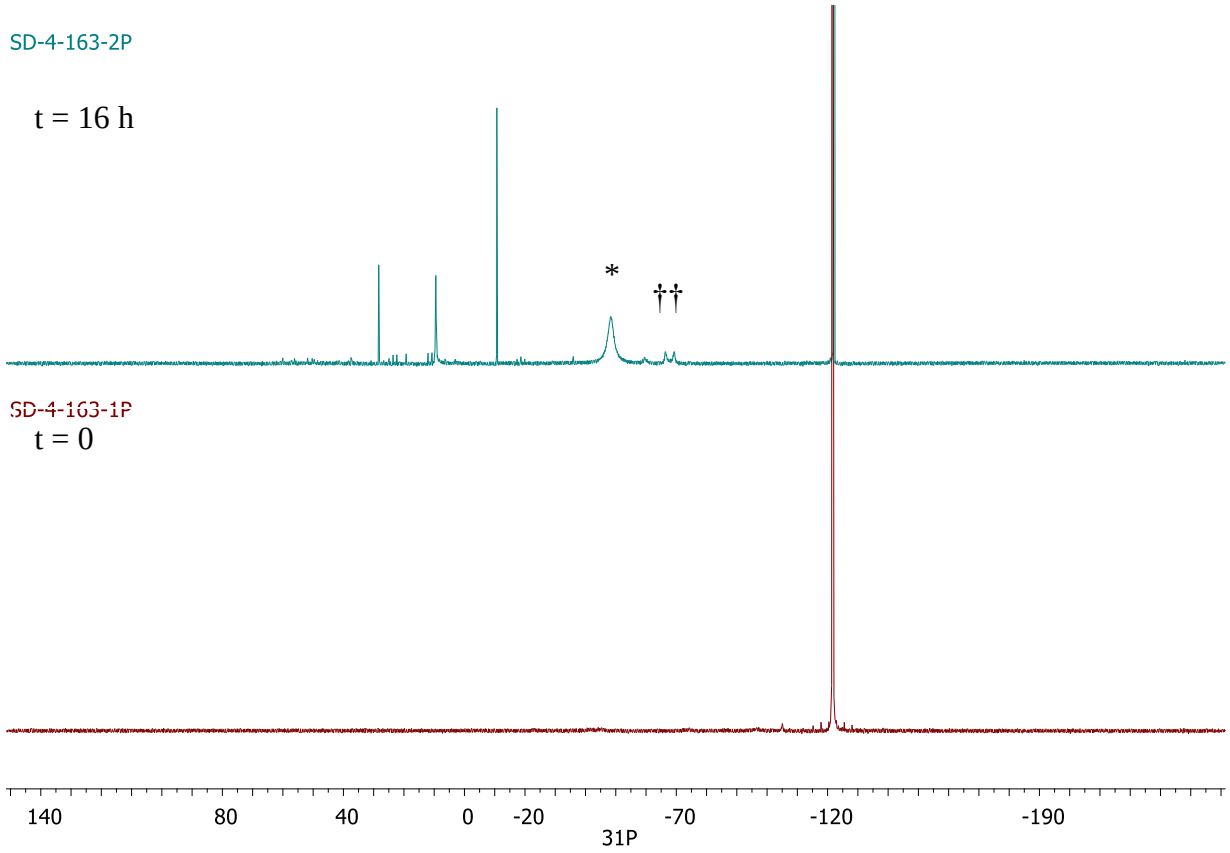
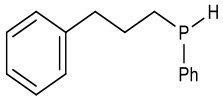


Figure S.44. $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of allyl benzene with three equiv. of diphenylphosphine by **1** – neat
Table 1, **3h**

Prepared according to the general procedure with the following modifications: 1) no solvent was used 2) three equiv. of diphenylphosphine was used 3) no initial ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra was obtained 4) After 24 h, 5 mg 1,3,5 trimethoxy-benzene was added and 0.5 ml of $CDCl_3$ was added to the NMR tube and ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra were obtained. 70% conversion to the hydrophosphination product was measured by $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra is in accordance with the previous reports.[22]

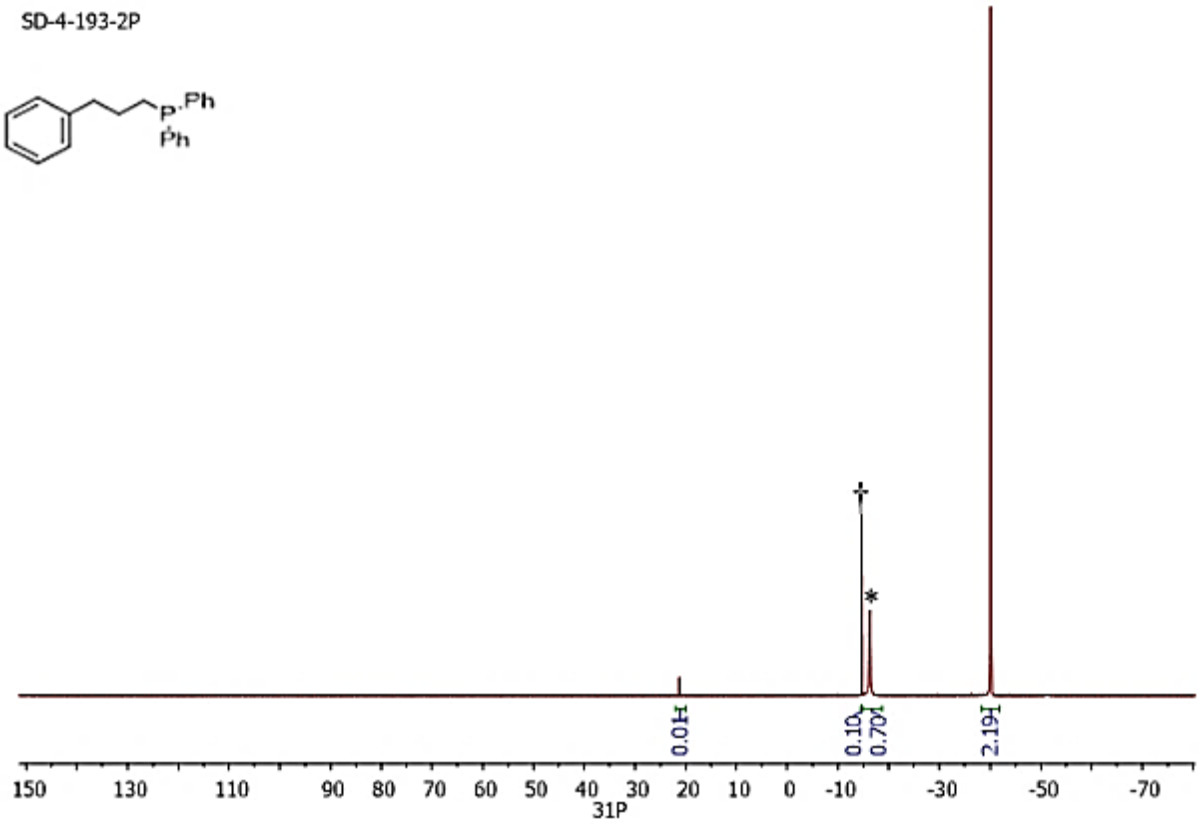


Figure S.45. ^{31}P NMR spectrum ($CDCl_3$, 202 MHz) at 24 h of 360 nm irradiation

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of allyl benzene with three equiv. of diphenylphosphine by **1** (continued)

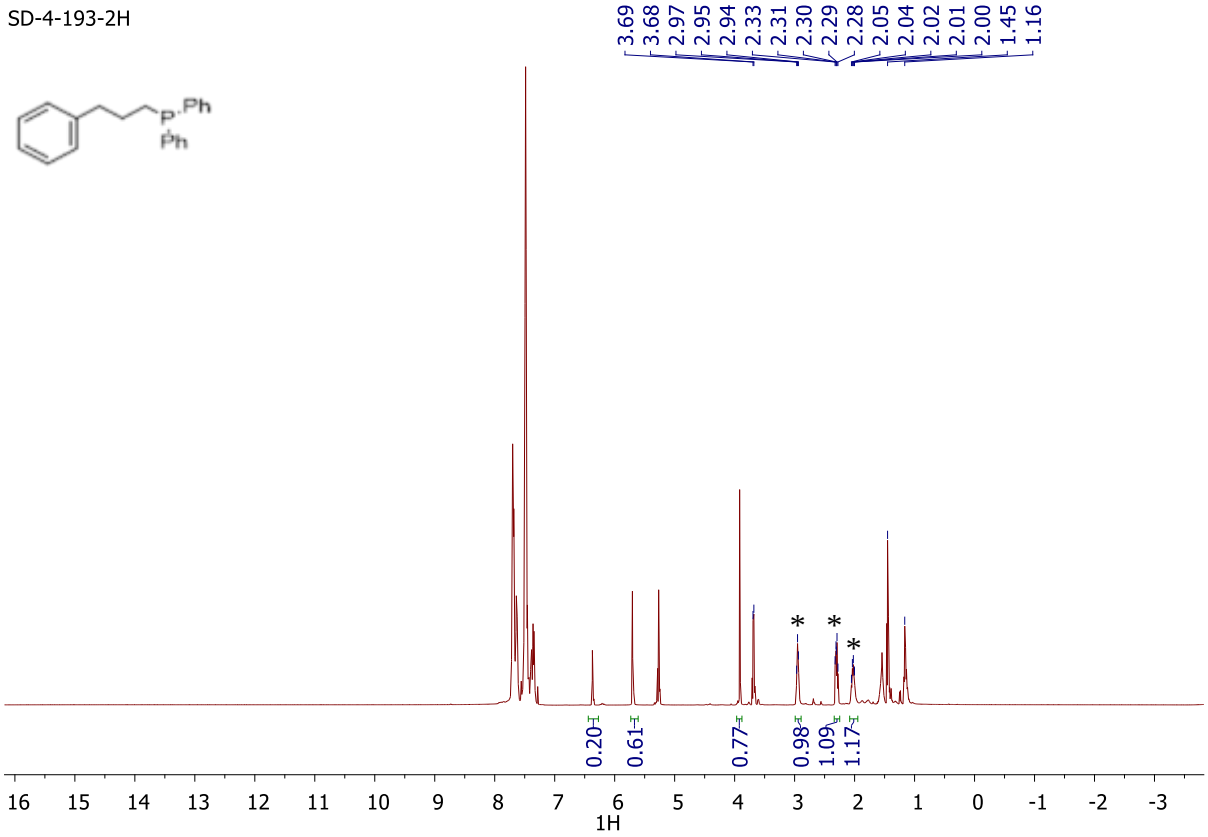


Figure S.46. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of trial 1 at t = 24 h of 360 nm irradiation

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of allyl chloride
Table 1, **3i**

Prepared according to the general procedure with two equiv. of phenylphosphine and an internal standard of 10 mg of 1,3,5-trimethoxybenzene. 75% conversion of allyl chloride was measure after 18 h as measured by ^{1}H NMR spectroscopy. 63% conversion was measured by integration to an internal standard of 1,3,5-trimethoxybenzene and by $^{31}P\{^{1}H\}$ NMR spectroscopy. $^{31}P\{^{1}H\}$ Spectra are consistent with previous literature reports.[23]

^{1}H spectra of this product is not previously reported. Purification of the crude product was achieved by flash column chromatography on silica gel with a 3:1 hexanes: DCM liquid phase but a small impurity persisted. The isolated yield of this product was 44% at 92% purity. The impurities were 4% of the double activation and 4% of an unknown product at -7 ppm in the $^{31}P\{^{1}H\}$NMR spectra.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.45 (m, 2H), 7.35 (m, 3H), 4.20 (d, *J* = 208.2 Hz, 1H), 3.72 – 3.33 (m, 2H), 2.20 – 1.75 (m, 4H)

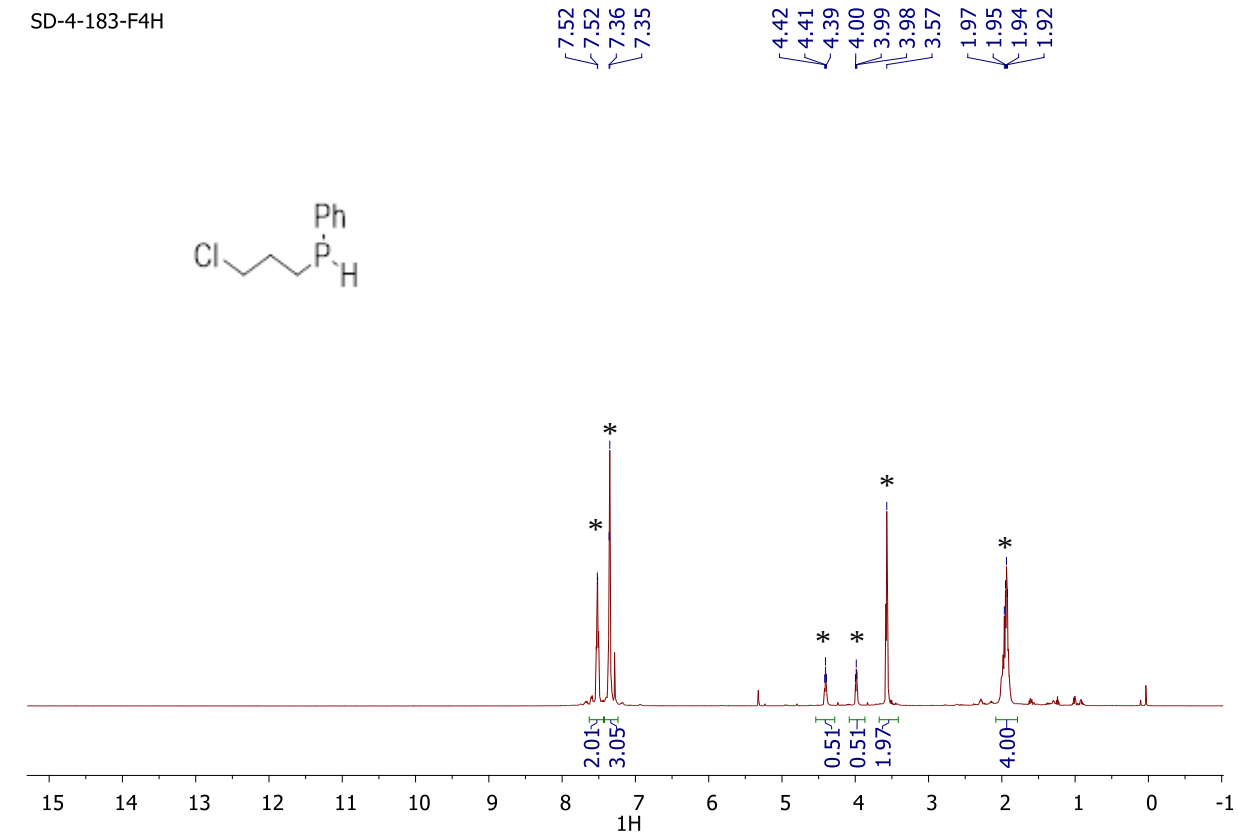


Figure S.47. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz)) at t = 18 h of 360 nm irradiation with catalyst removed by

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of allyl chloride with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

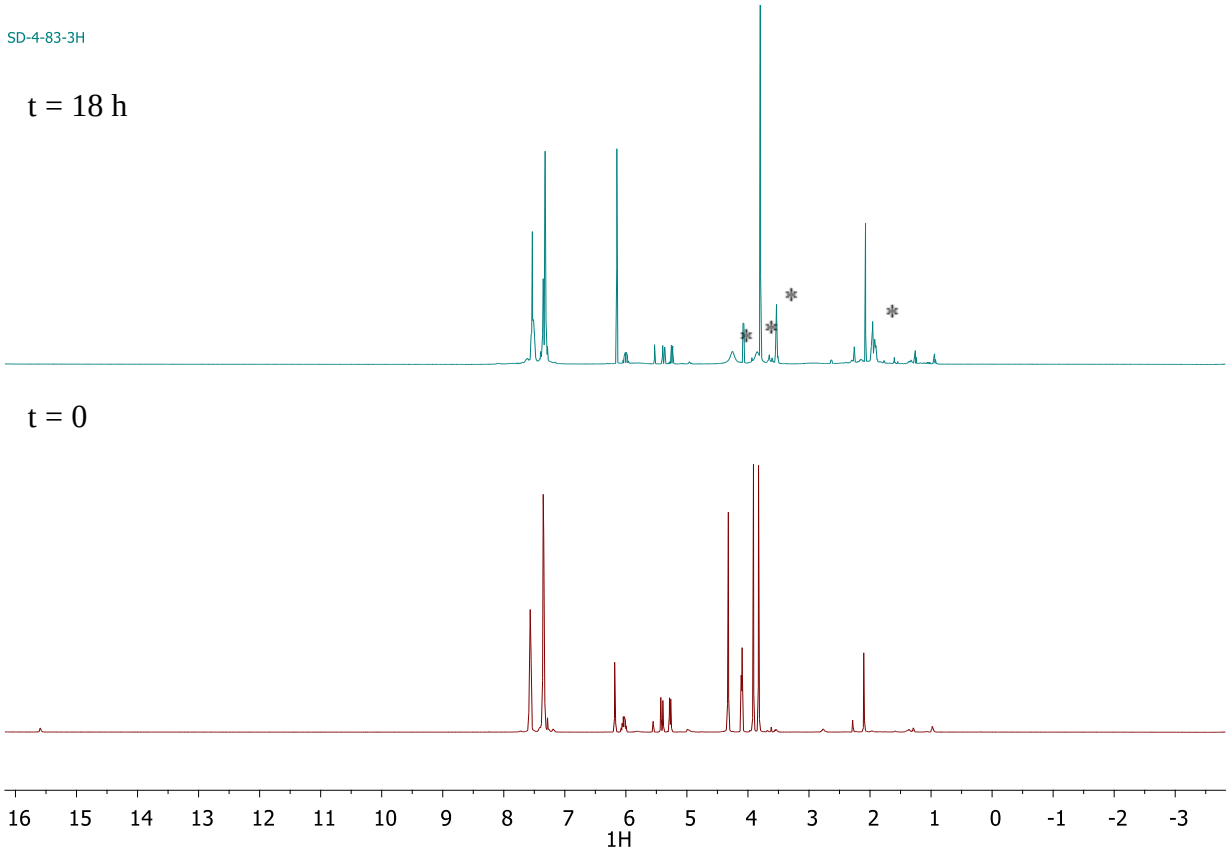
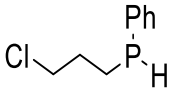


Figure S.48. Stacked ^{1}H NMR spectrum ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of allyl chloride with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued**)**

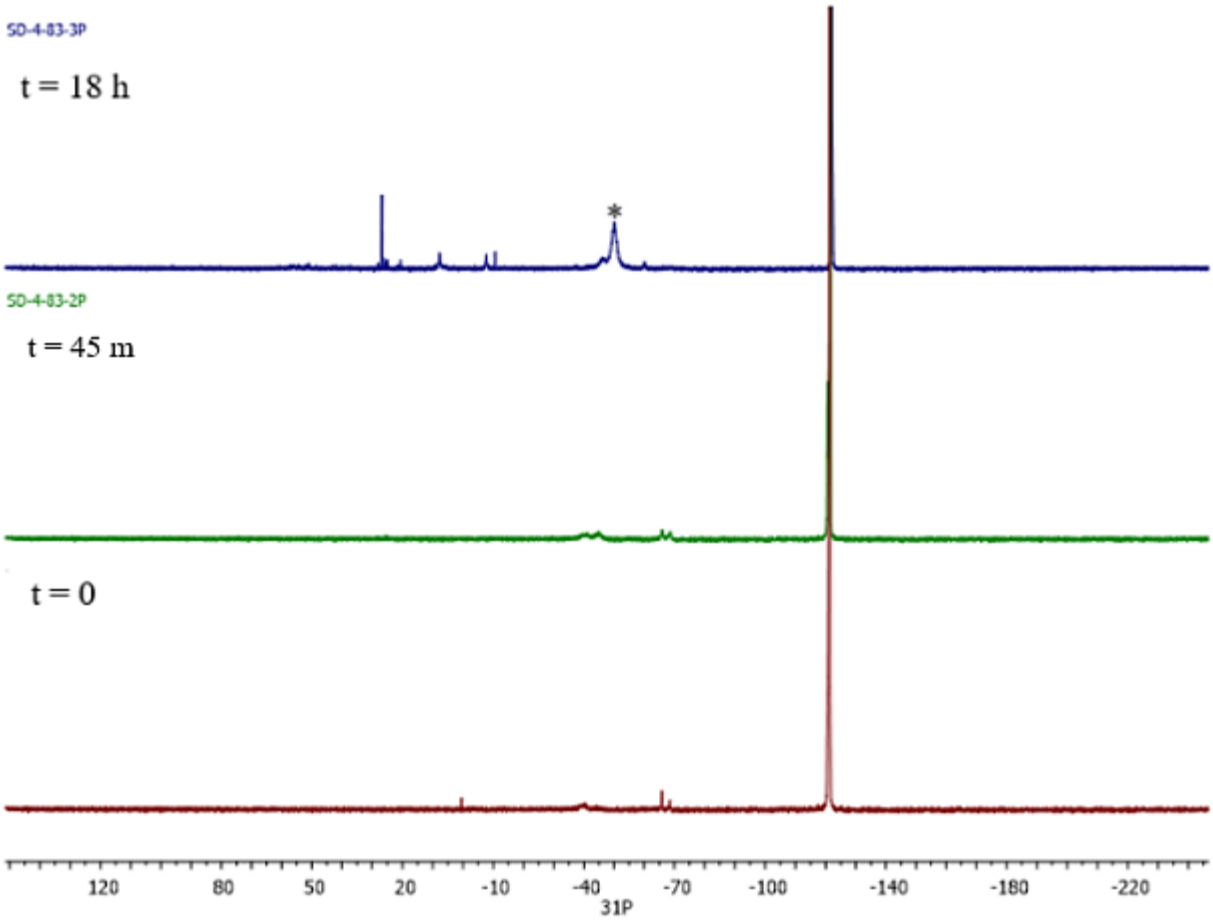
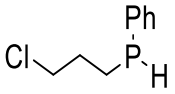


Figure S.49. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz) at t = 18 h of 360 nm irradiation



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of β-methyl styrene
Table 2, **4a**

Prepared by the general procedure with two equiv. of phenylphosphine and a 50:50 mixture of E:Z isomers of β-methyl styrene. 100% conversion was observed at 20 h of 360 nm irradiation as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy.

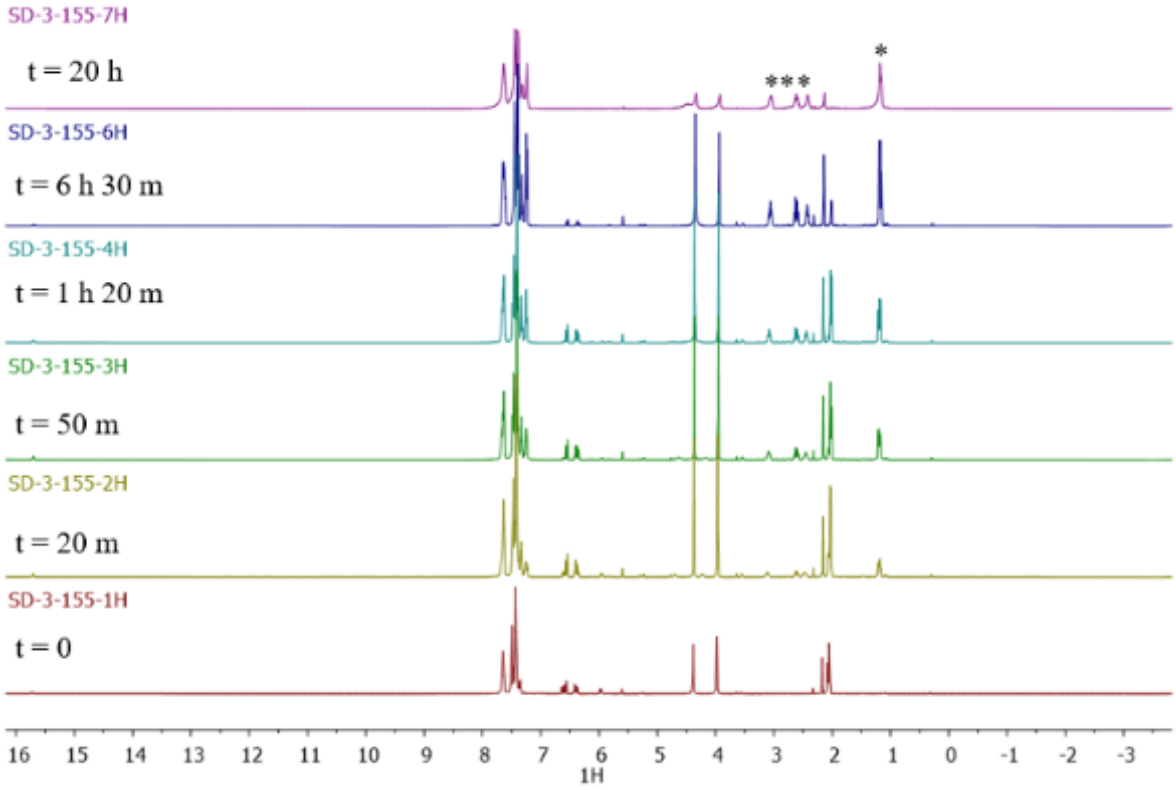
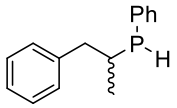


Figure S.50. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of β-methyl styrene with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

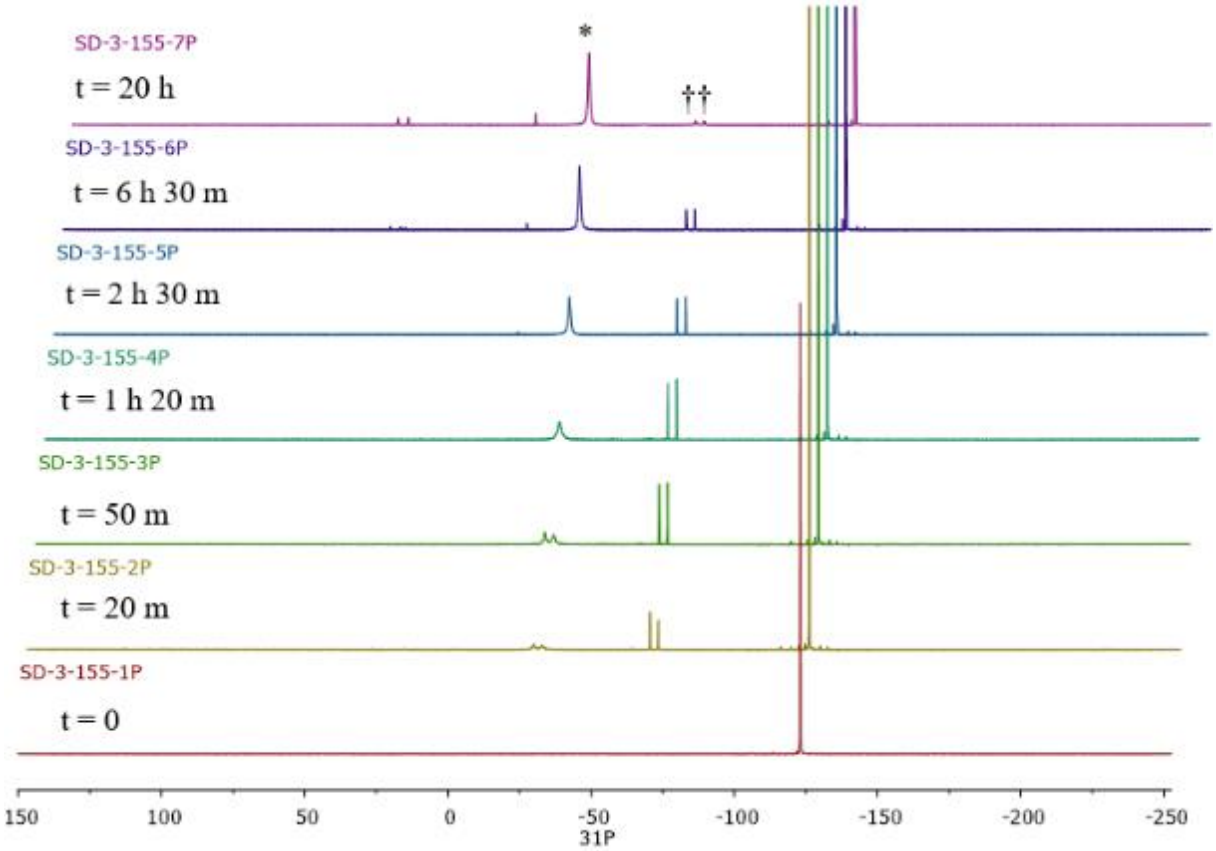
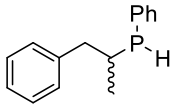


Figure S.51. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of α-methyl styrene with two equiv. of phenylphosphine by **1**
Table 2, **4b**

Prepared according to the general procedure with two equiv. of phenylphosphine**.** 92% conversion of α-methyl styrene was measure after 2 h and 15 min as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. 100% conversion was measured at 5 h of 360 nm irradiation. Spectra are consistent with previous reports.[6]

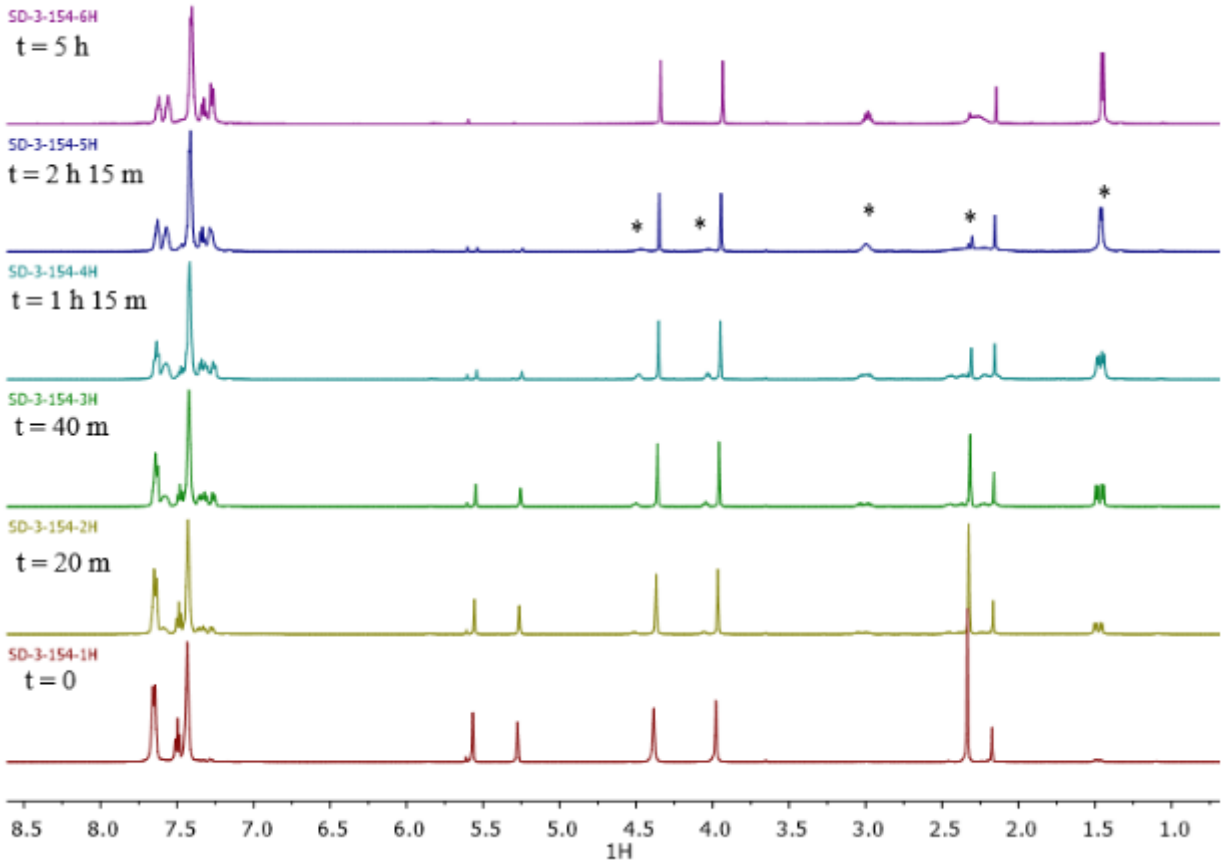
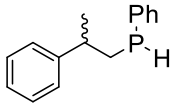


Figure S.52. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz). P-H protons are broadened into baseline in final spectra due to interaction with copper.



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of α-methyl styrene with two equiv. of phenylphosphine with 5 mol % of **1** under 360 nm irradiation (continued)

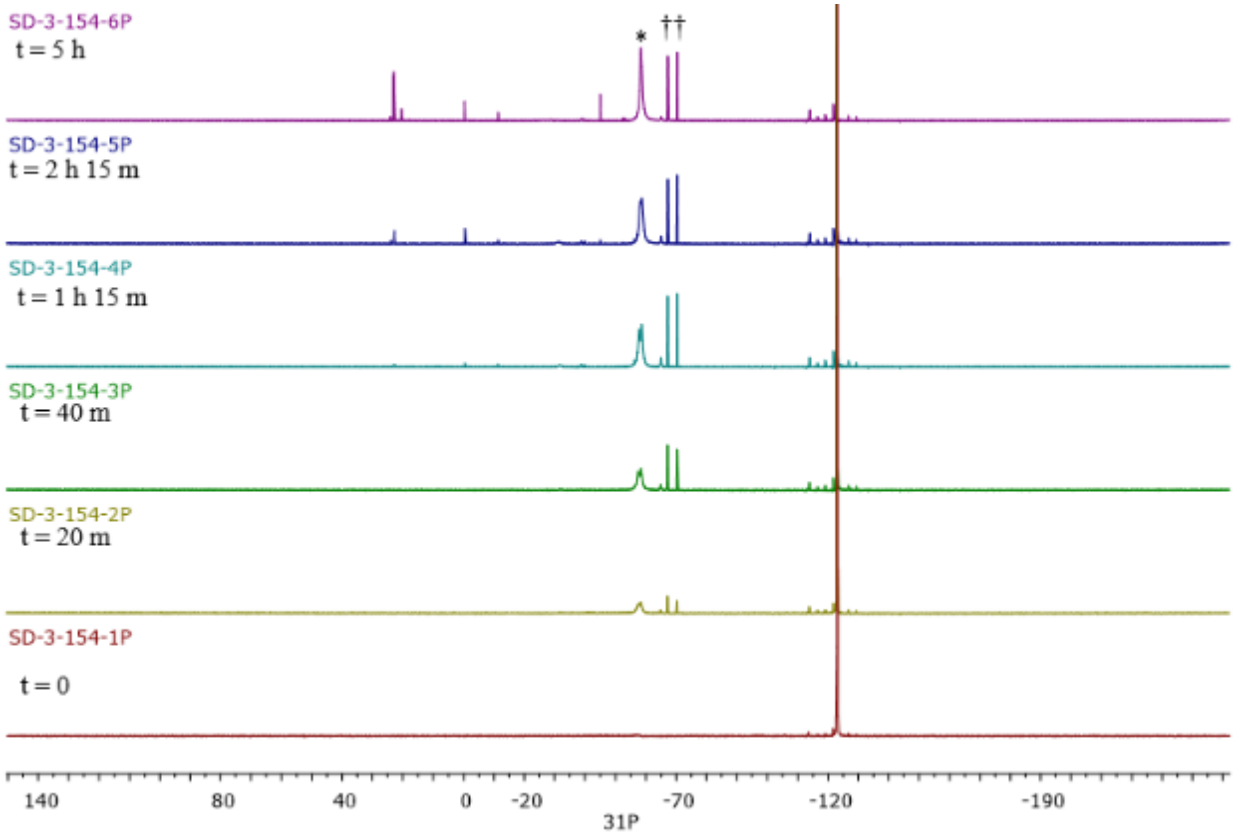
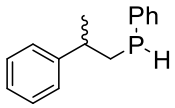


Figure S.53. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of α-methyl styrene
Table 2, **4c**

Prepared by the general procedure with modified starting material amounts of 0.25 mmol (29.5 mg) α-methyl styrene, 0.375 mmol (70 mg) diphenylphosphine and 3.2 mg (0.0125 mmol, 5 mol %) **1** and 5 mg (0.03 mmol) of 1,3,5-trimethoxybenzene. 83% conversion was measured after 20 h of 360 nm irradiation as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[8]

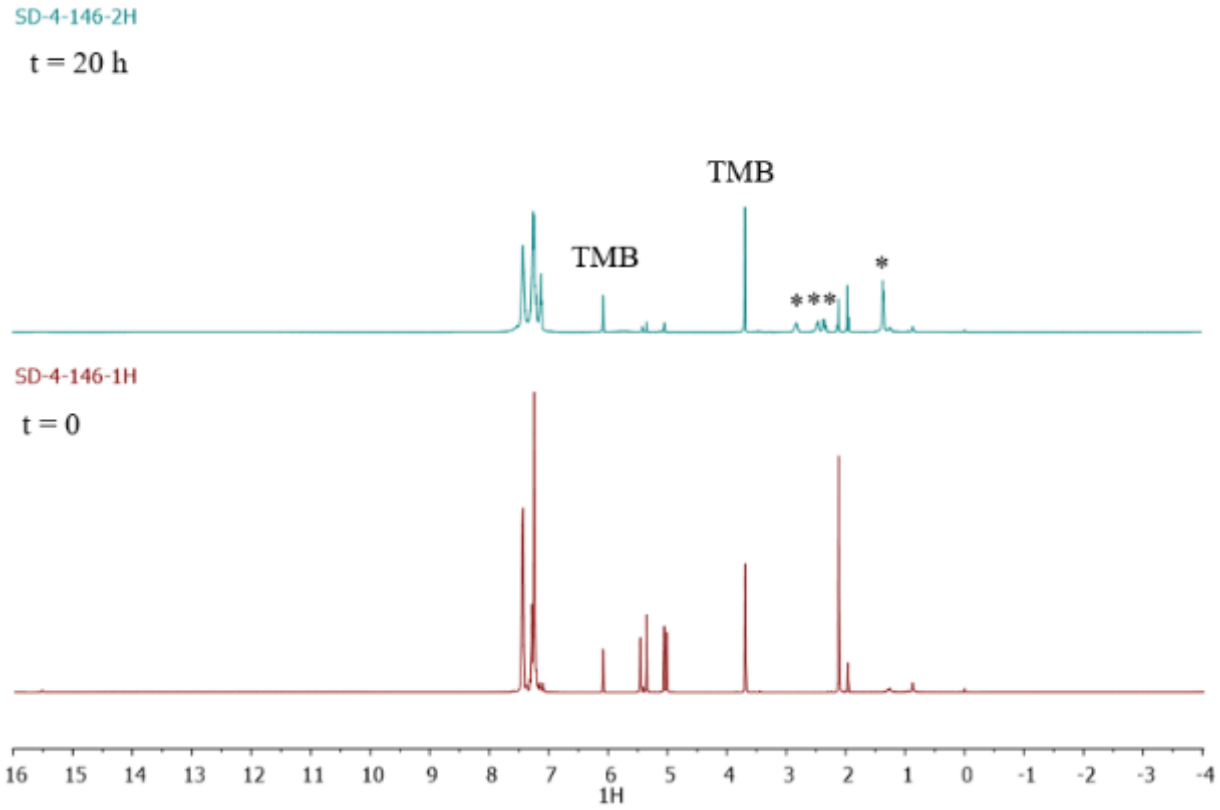
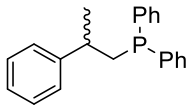


Figure S.54. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of α-methyl styrene with 1.5 equiv. of diphenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

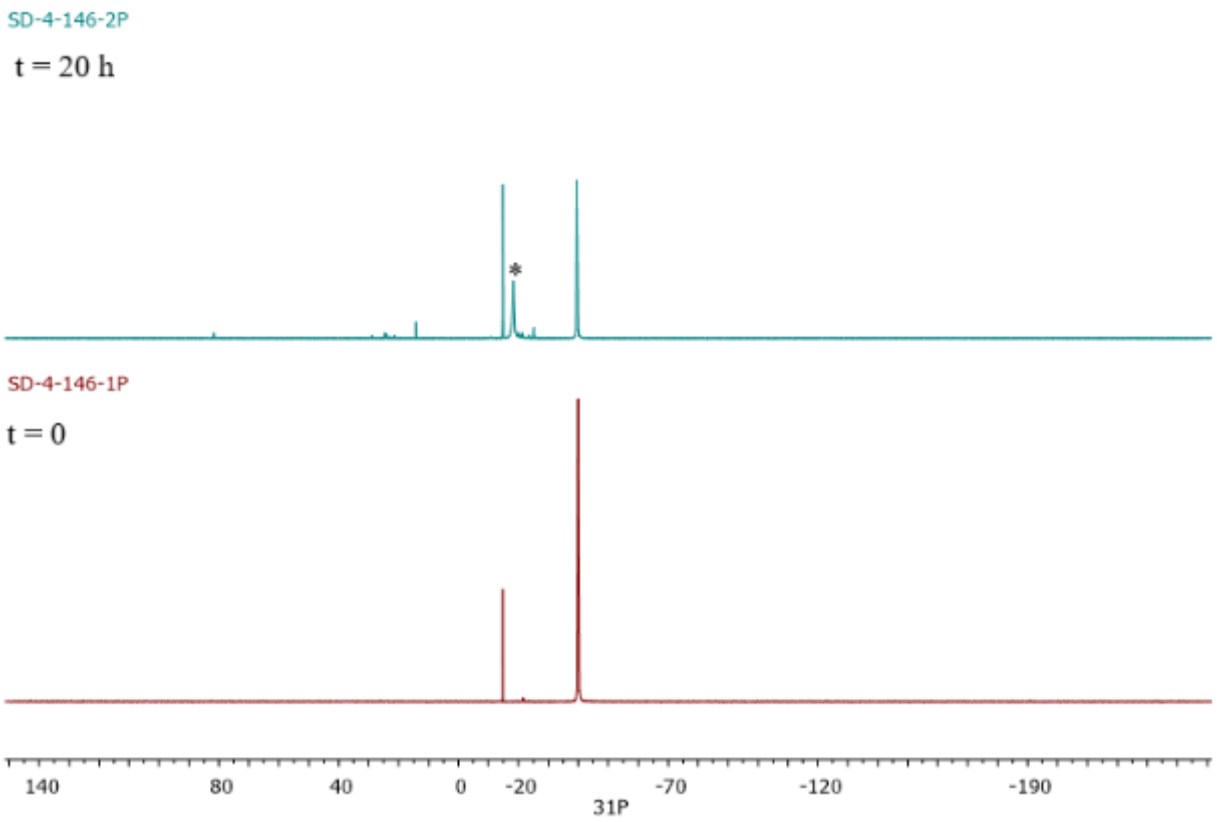
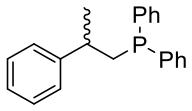


Figure S.55. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 2,3-dimethyl,1-3-butadiene
Table 2, **4d**

Prepared according to the general procedure with two equiv. of phenylphosphine. 100% conversion of 2,3-dimethyl,1-3-butadiene was observed after 1 h 20 min of 360 nm irradiation as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[5]

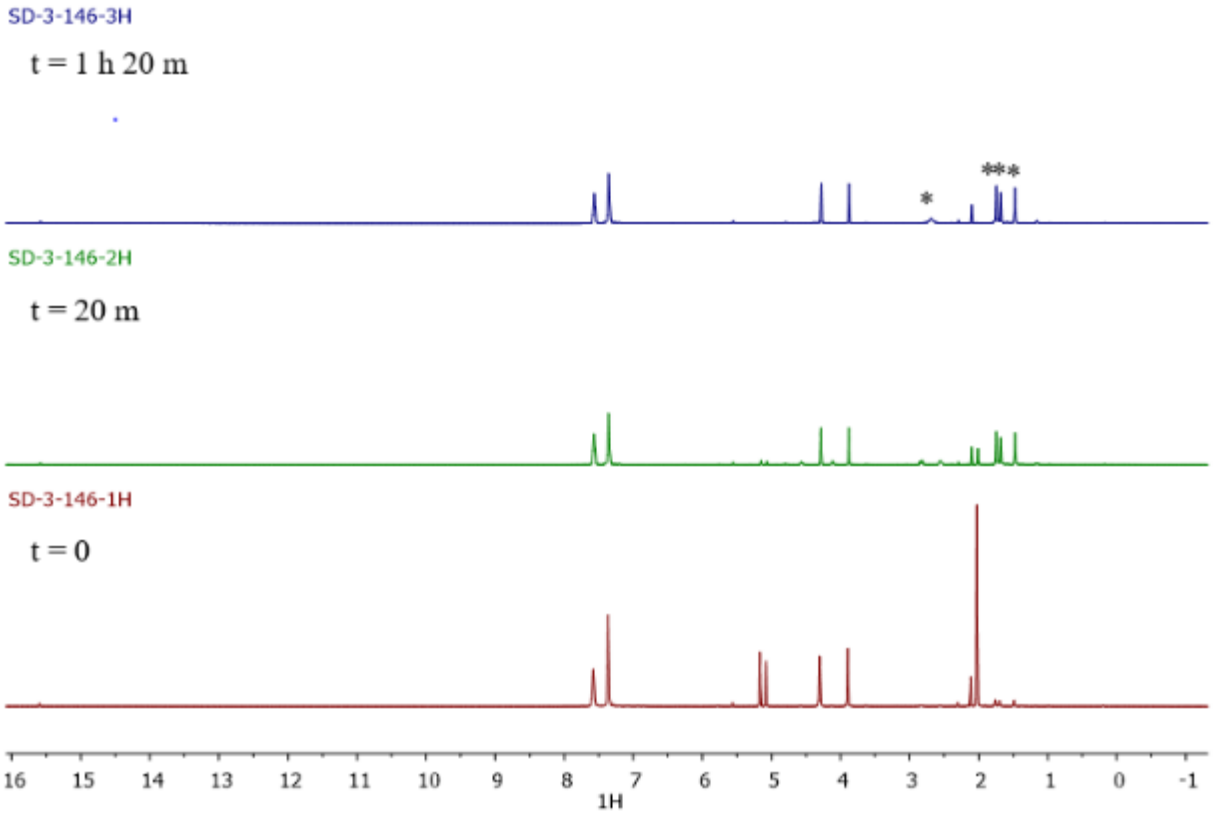
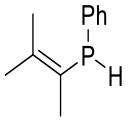


Figure S.56. Stacked ^{1}H NMR ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 2,3-dimethyl,1-3-butadiene with two equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

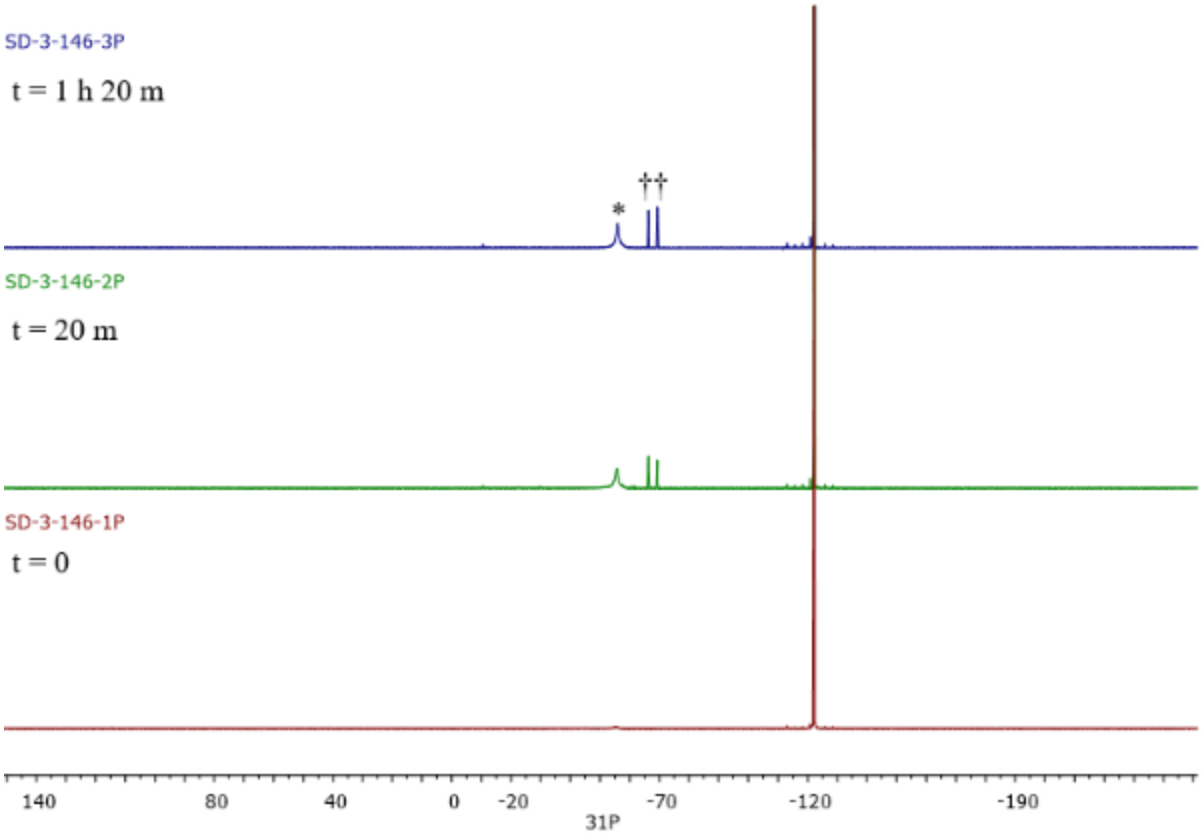
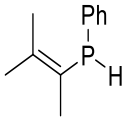


Figure S.57. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 2,3-dimethyl,1-3-butadiene with one equiv. of diphenylphosphine by **1**
Table 2, **4e**

Prepared according to general procedure with one equiv. of diphenylphosphine. 100% conversion of 2,3-dimethyl,1-3-butadiene was measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy after 8 h of 360 nm irradiation. Spectra is in accordance with previous reports.[21]

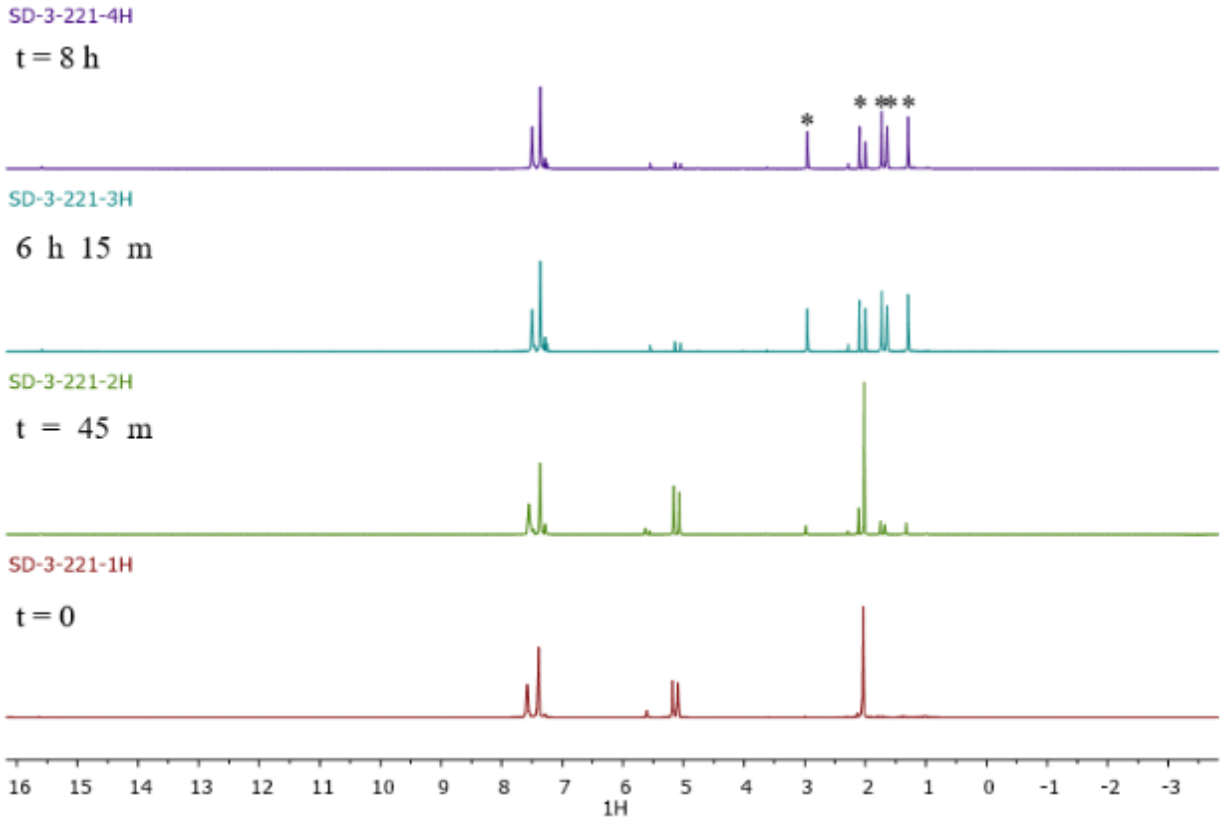
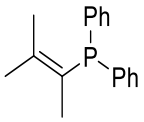


Figure S.58. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 2,3-dimethyl,1-3-butadiene with one equiv. of diphenylphosphine and 5 mol % of **1** under 360 nm irradiation (continued)

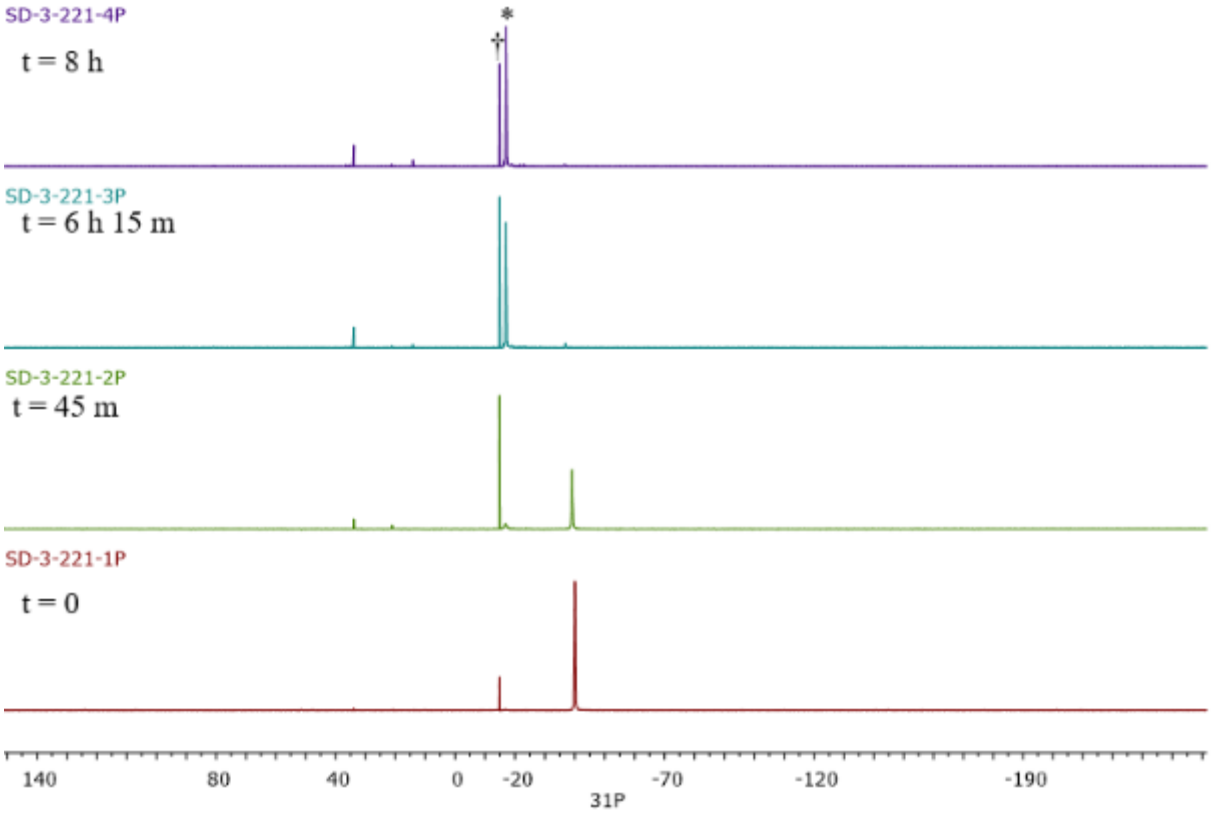
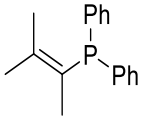


Figure S.59. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of norbornene
Table 2, **4f**

Prepared according to the general procedure with two equiv. of phenylphosphine. Greater than 99% of norbornene was converted after 50 min of 360 nm irradiation as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous literature reports.[5]

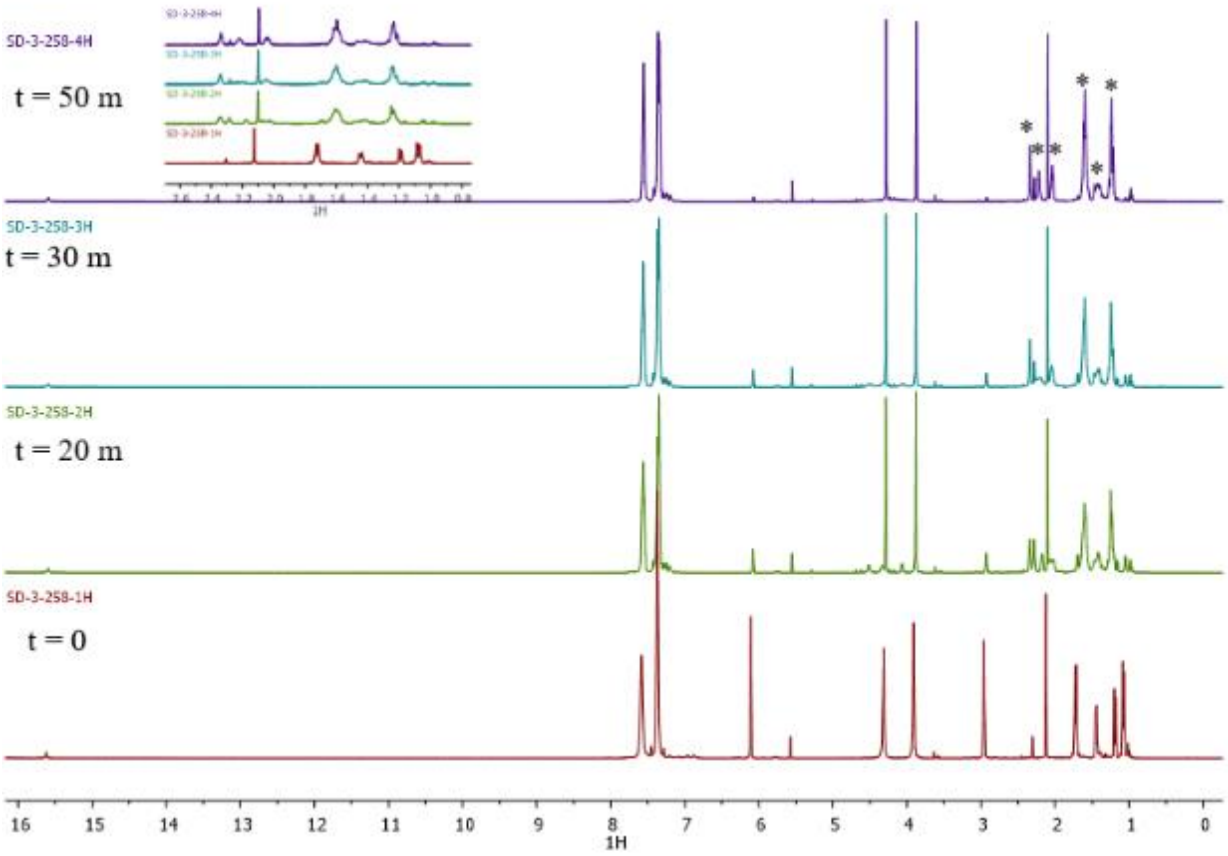
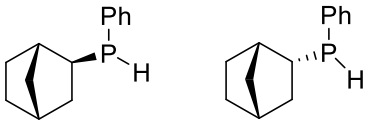


Figure S.60. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of norbornene with two equiv. of phenylphosphine with 5 mol % of **1** under 360 nm irradiation (continued)

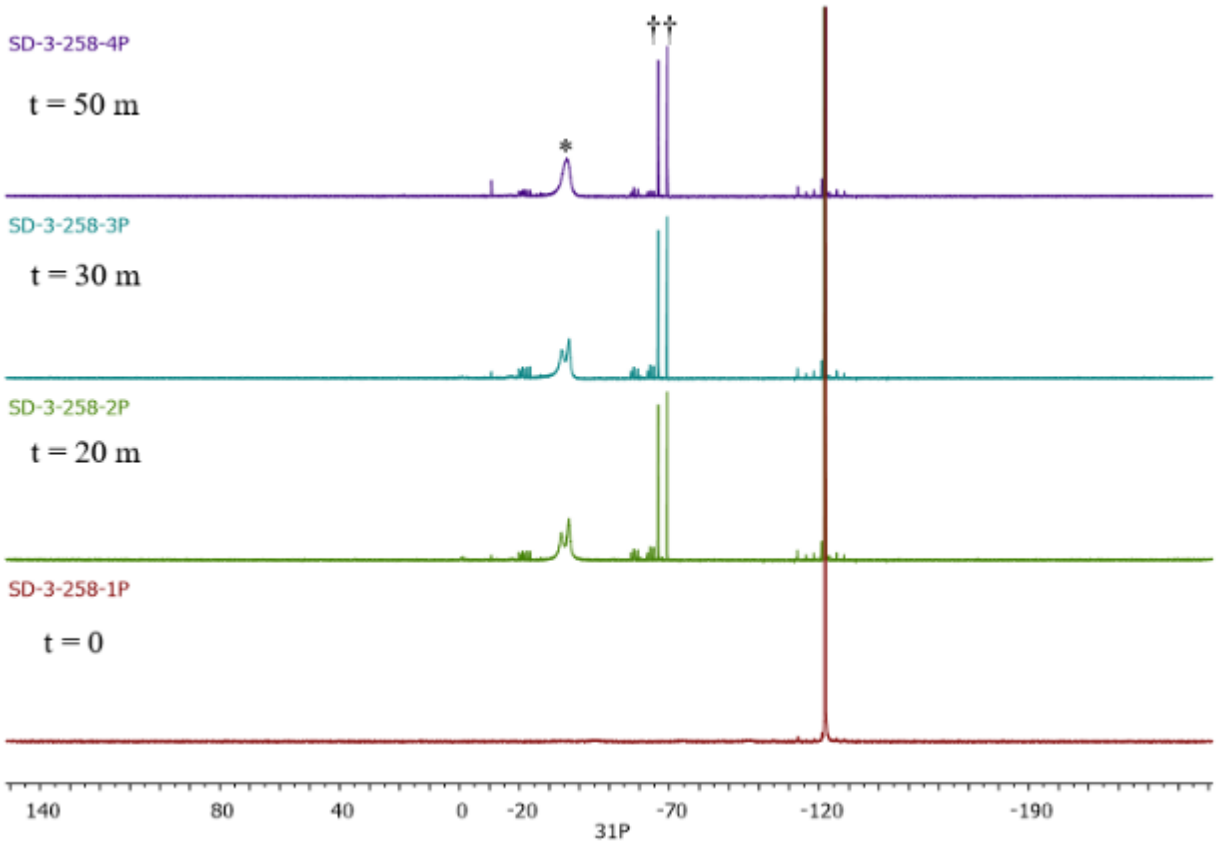
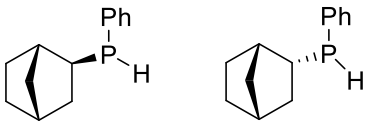


Figure S.61. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of acrylonitrile
Table 2, **4g**

Prepared according to the general procedure with two equiv. of phenylphosphine and the modification that it was not irradiated because the initial ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra indicated 100% conversion of acrylonitrile. Spectra are consistent with previous reports.[5]

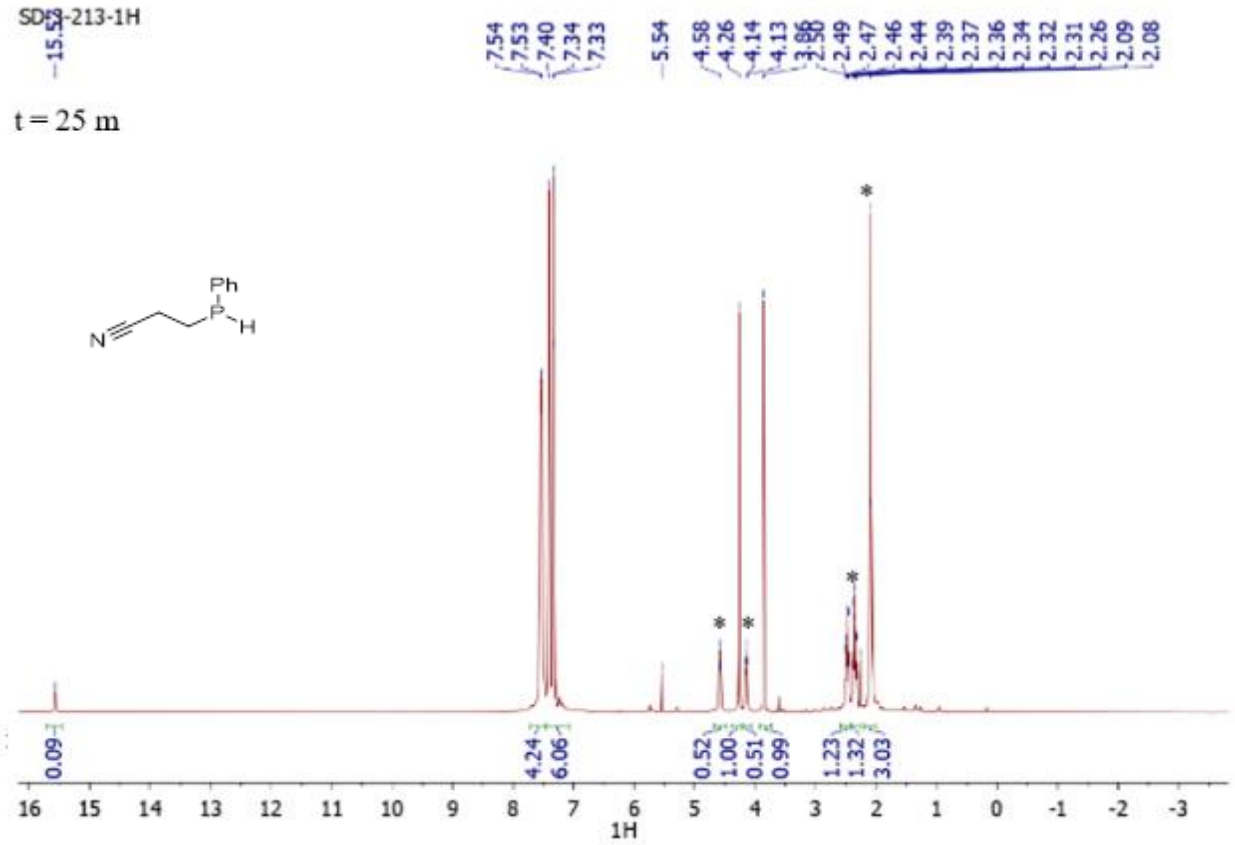


Figure S.62. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) at t = 25 min

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of acrylonitrile with two equiv. of phenylphosphine by 5 mol % of **1** (continued)

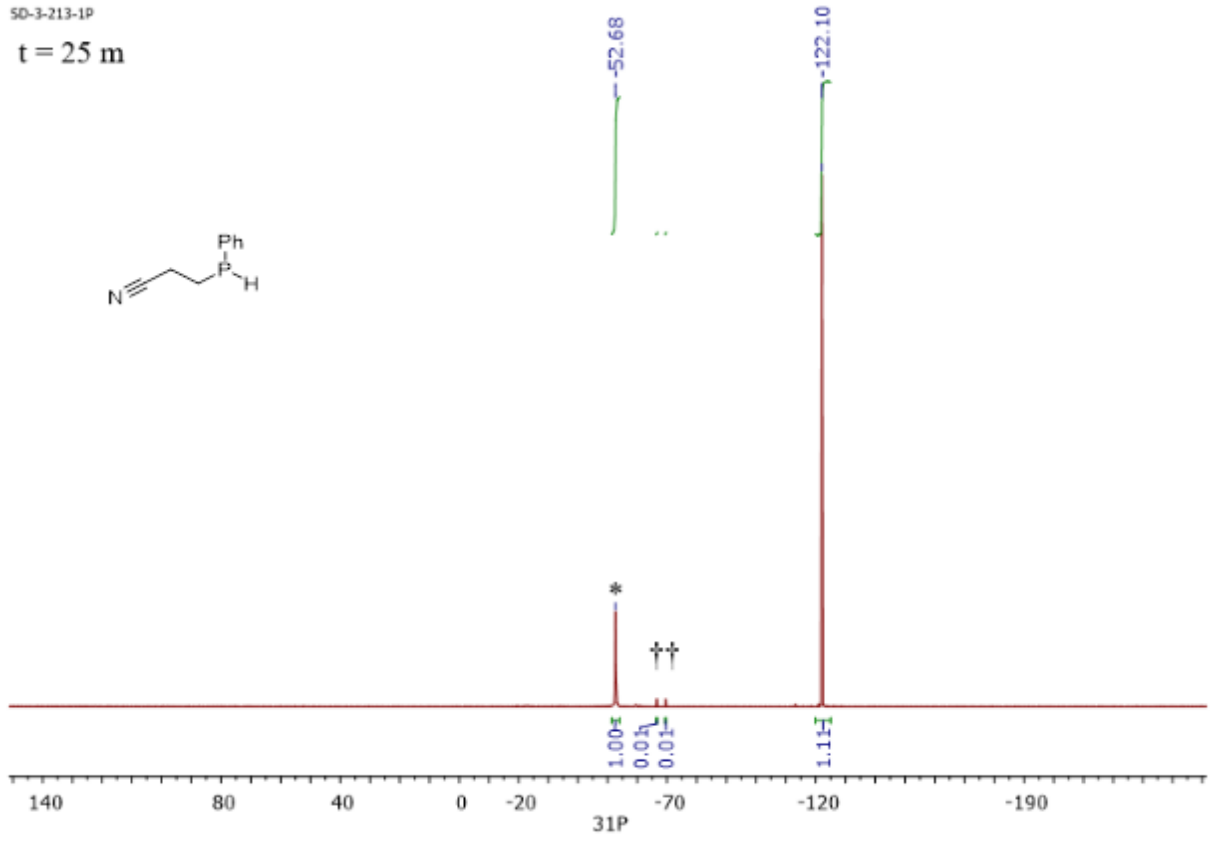


Figure S.63. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 202 MHz) at t = 25 min

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of acrylonitrile with one equiv. of diphenylphosphine by **1**
Table 2, **4h**

Prepared according to the general procedure with one equiv. of diphenylphosphine and the modification that it was not irradiated because the initial ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra indicated 98% conversion of acrylonitrile as measured by ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[21]

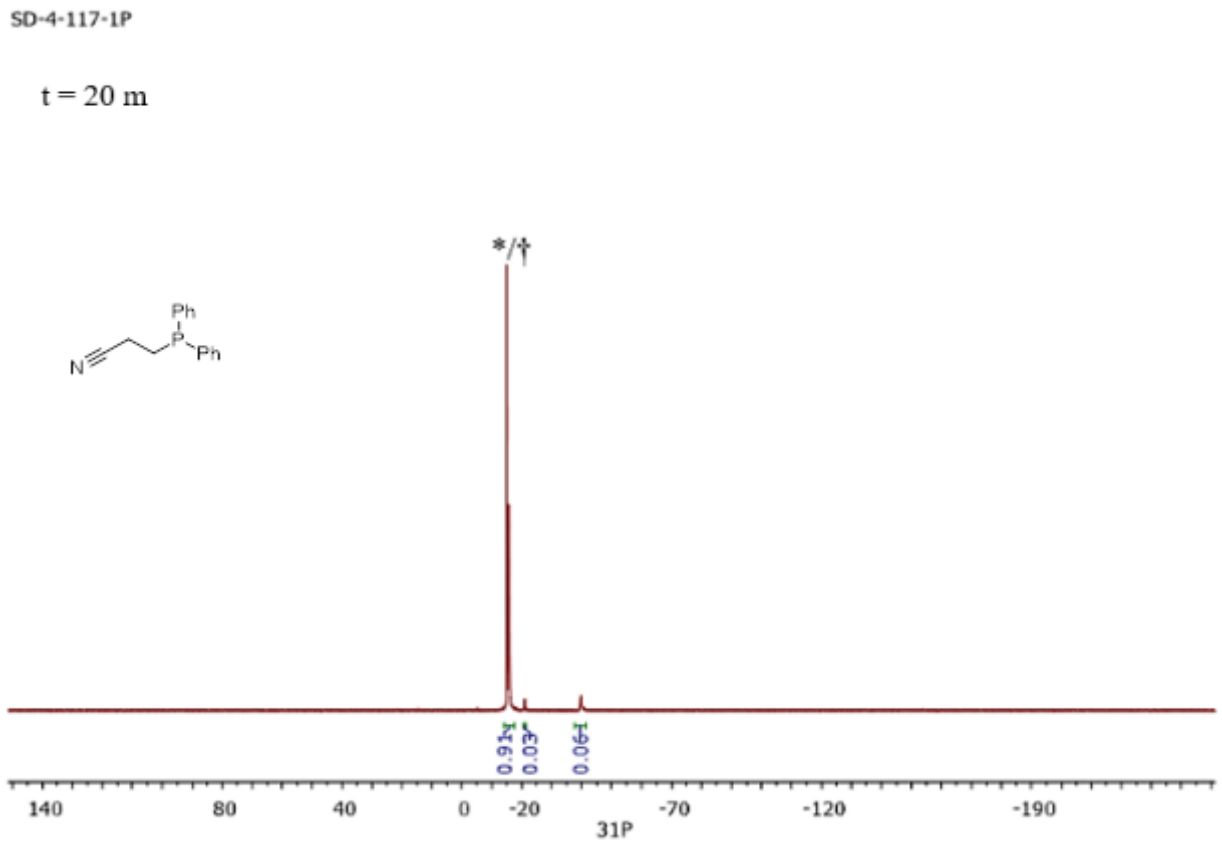


Figure S.64. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 202 MHz) at t = 20 min

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of methylacrylate
Table 2, **4i**

Prepared according to the general procedure with two equiv. of phenylphosphine and the modification that it was not put under 360 nm irradiation because the reaction went to 99% completion by the initial ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra. Spectra are consistent with previous reports.[5]

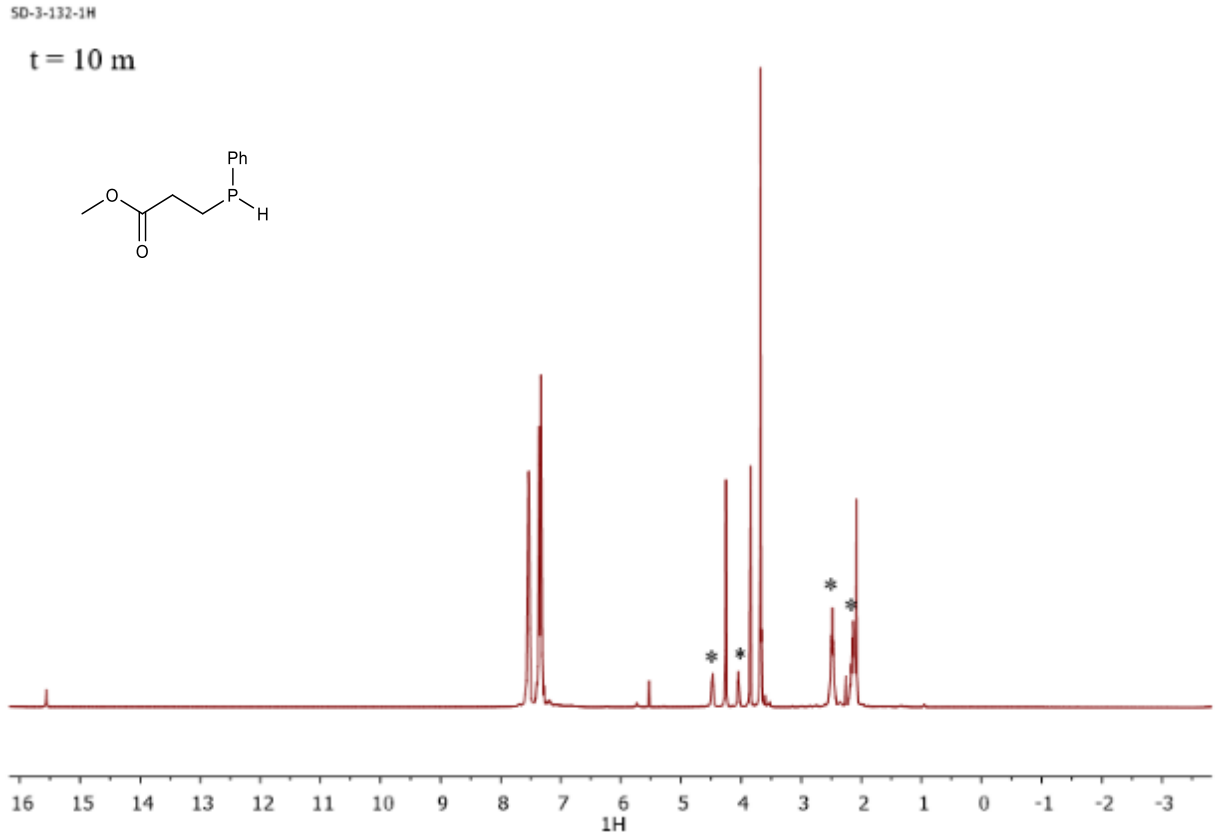


Figure S.65. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) at t = 10 min

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of methyl acrylate with two equiv. of phenylphosphine by 5 mol % of **1** (continued)

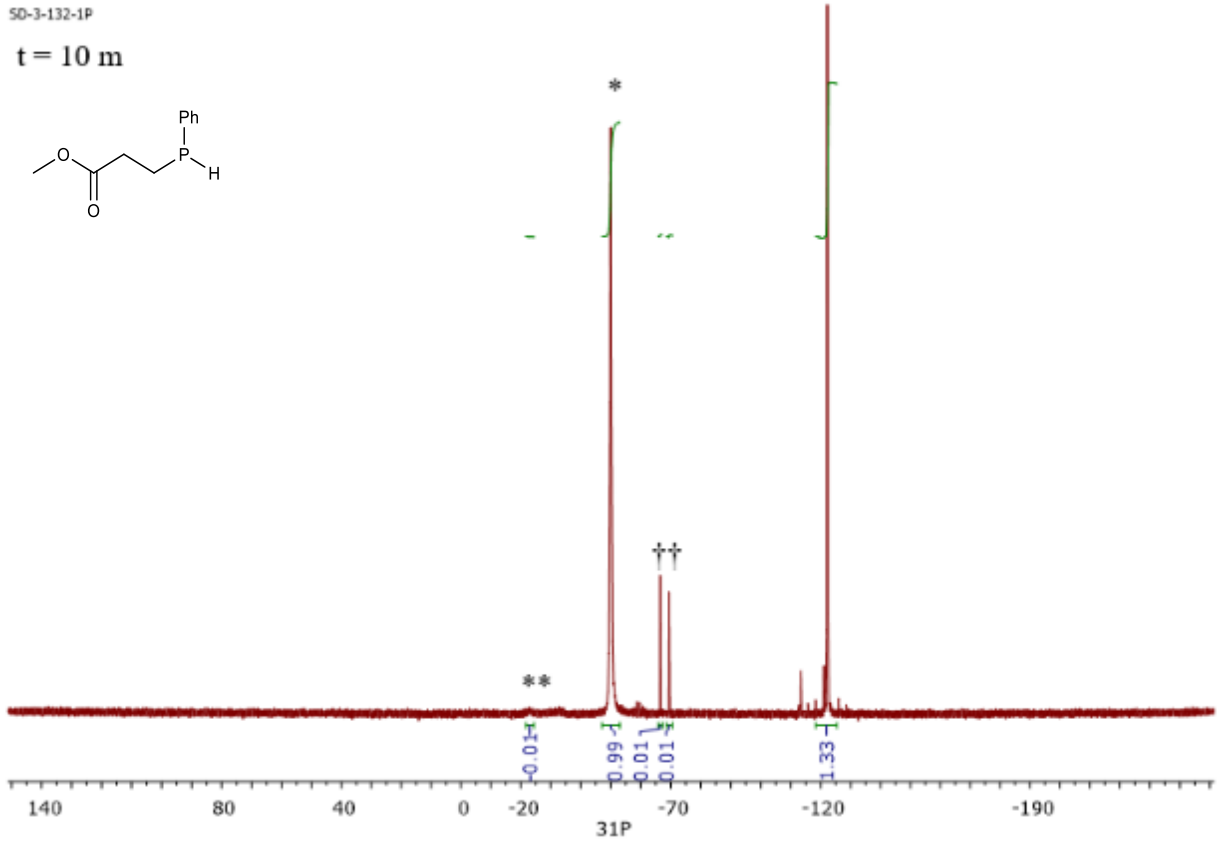


Figure S.66. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 202 MHz) at t = 10 m

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of methylacrylate with one equiv. of diphenylphosphine by **1**
Table 2, **4j**

Prepared according to the general procedure with one equiv. of diphenylphosphine and the modification that it was not put under 360 nm irradiation because the reaction went to 99% completion by the initial ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra. Spectra are consistent with previous reports. [21]

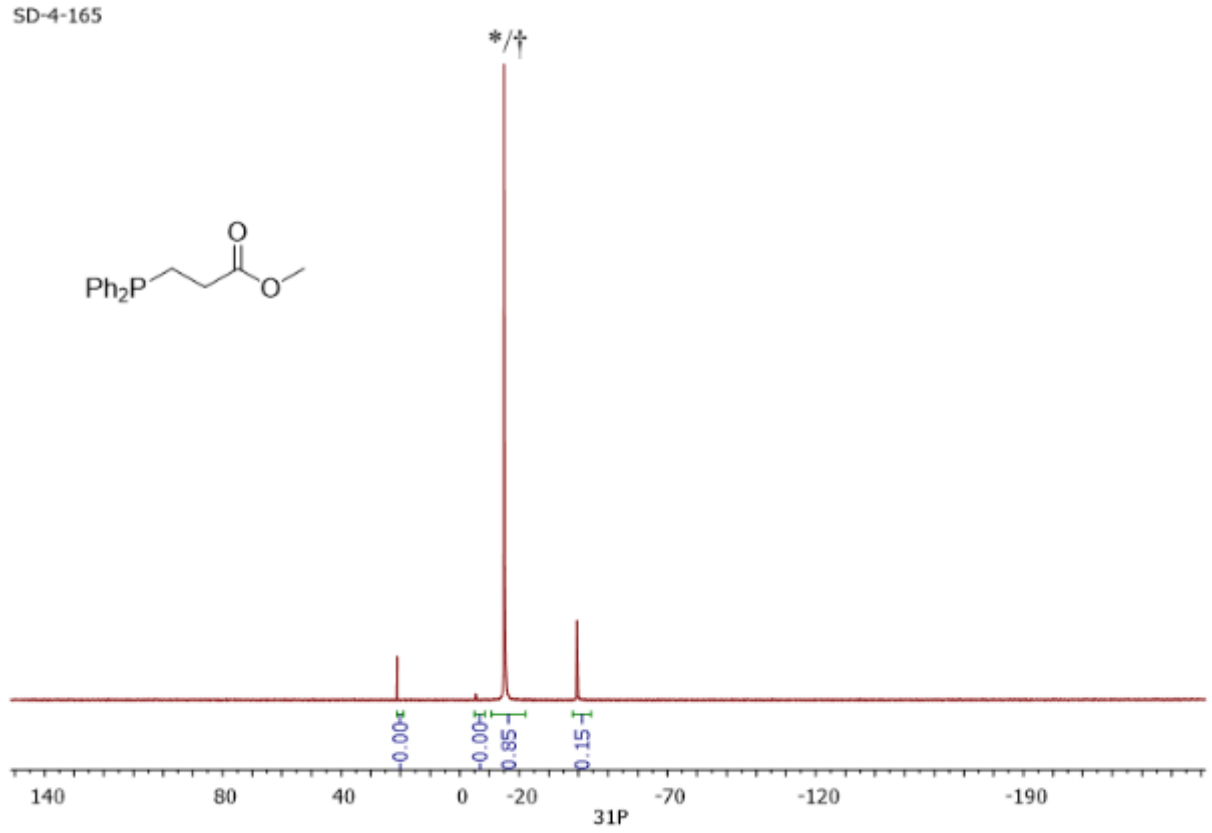


Figure S.67. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$, 202 MHz) at t = 15 min

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-phenyl-1-butyne
Eqn (4)

Prepared according to the general procedure with one equiv. of phenylphosphine and an external standard of PPh_3. 80% of 1-phenyl-1-butyne was converted after 24 h of 360 nm irradiation with 3:1 *Z:E* selectivity as measured by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[4]

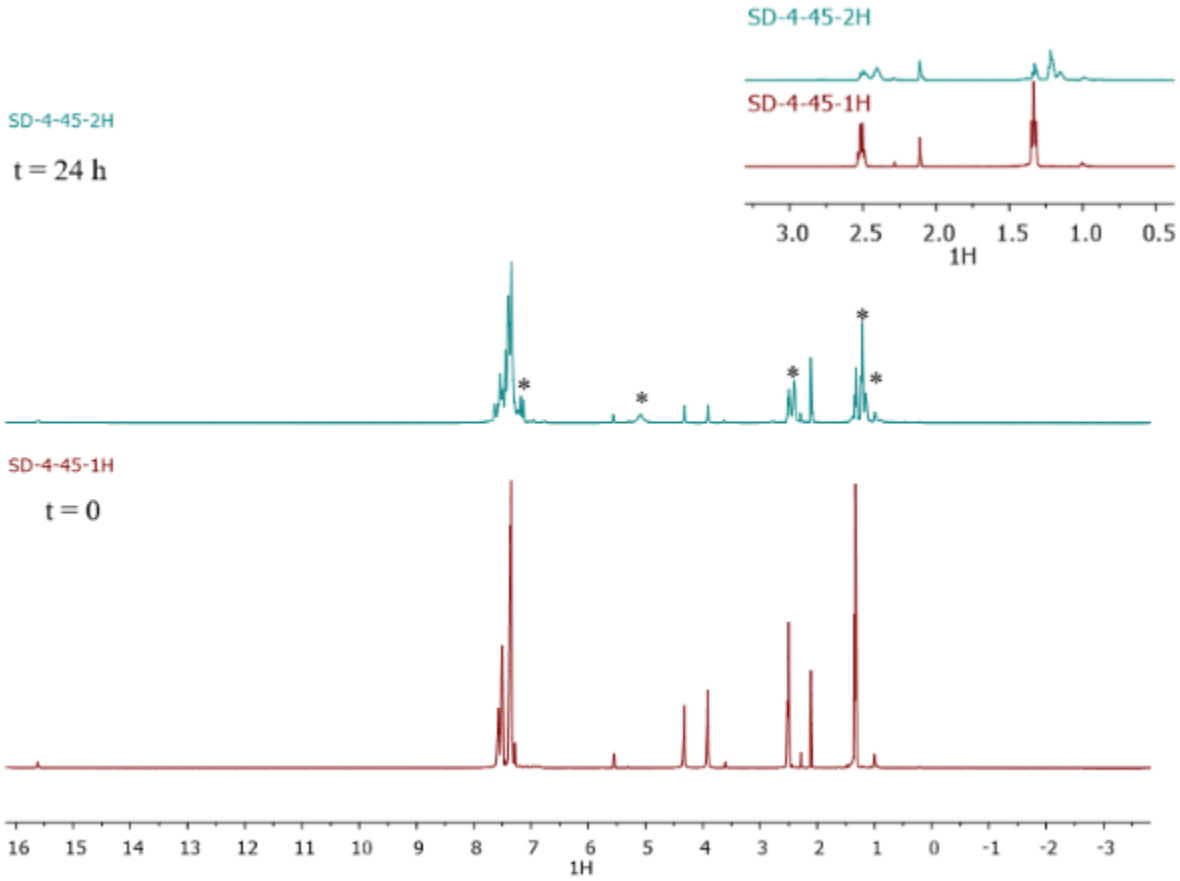
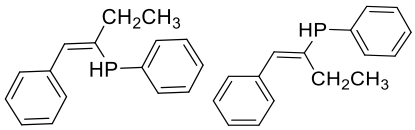


Figure S.68. Stacked ^1H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-phenyl-1-butyne with one equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

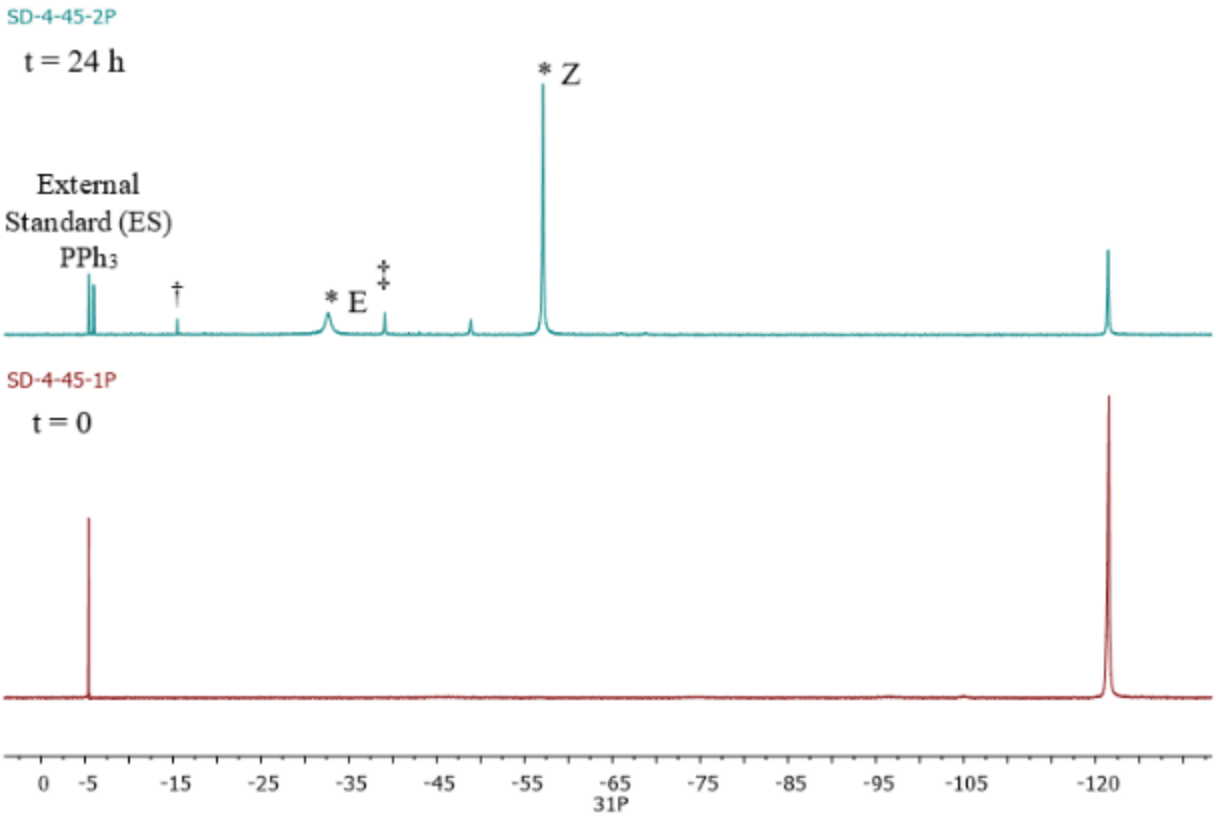
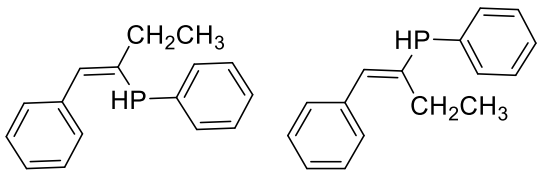


Figure S.69. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz). ‡ Consitent with double hydrophosphination product.



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-phenyl-1-butyne with one equiv. of diphenylphosphine by **1**
Eqn (4) and Table S3

Prepared in accordance with the general procedure with one equiv. of diphenylphosphine. 74% conversion of 1-phenyl-1-butyne with 1:1.1 *Z:E* selectivity was measured after 24 h of 360 nm irradiation. In Trial 2, 75% conversion was observed with 4.8:1 *Z:E* selectivity. The inconsistency is likely due to isomerization under UV light[4] or on metal isomerization.[24]

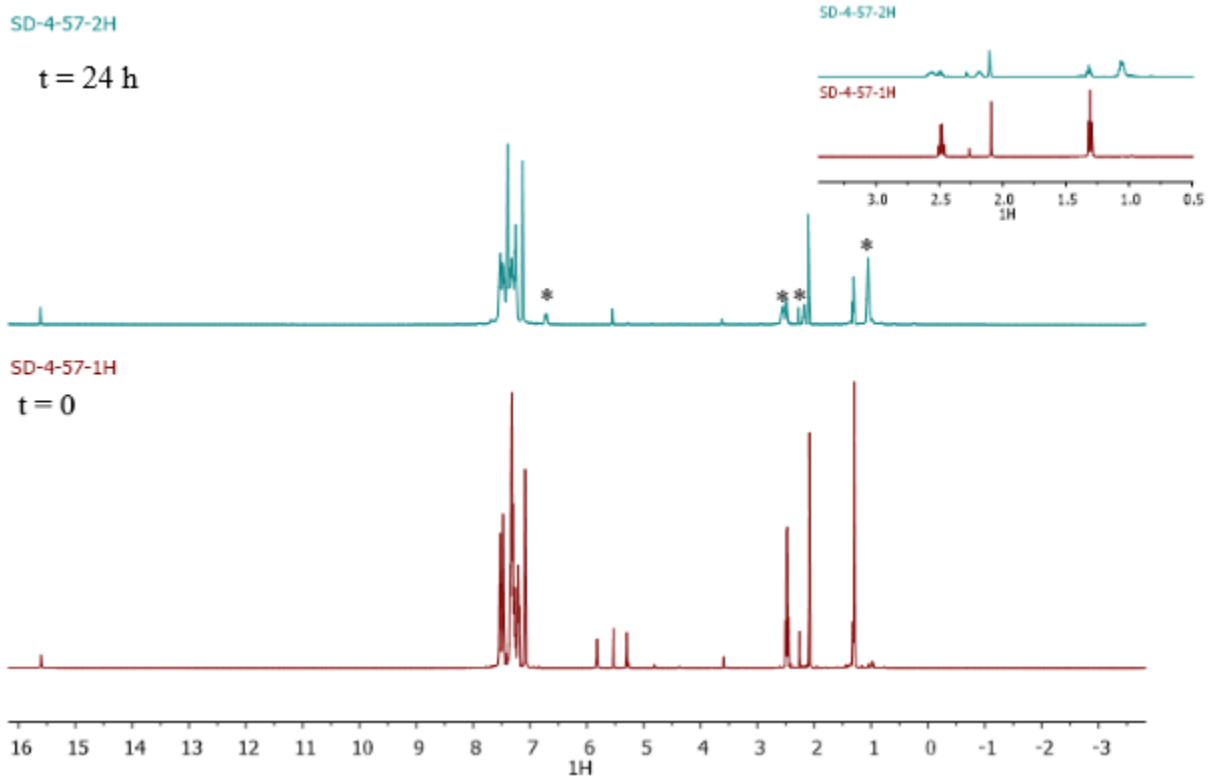
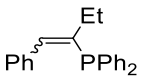


Figure S.70. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 1-phenyl-1-butyne with one equiv. of diphenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

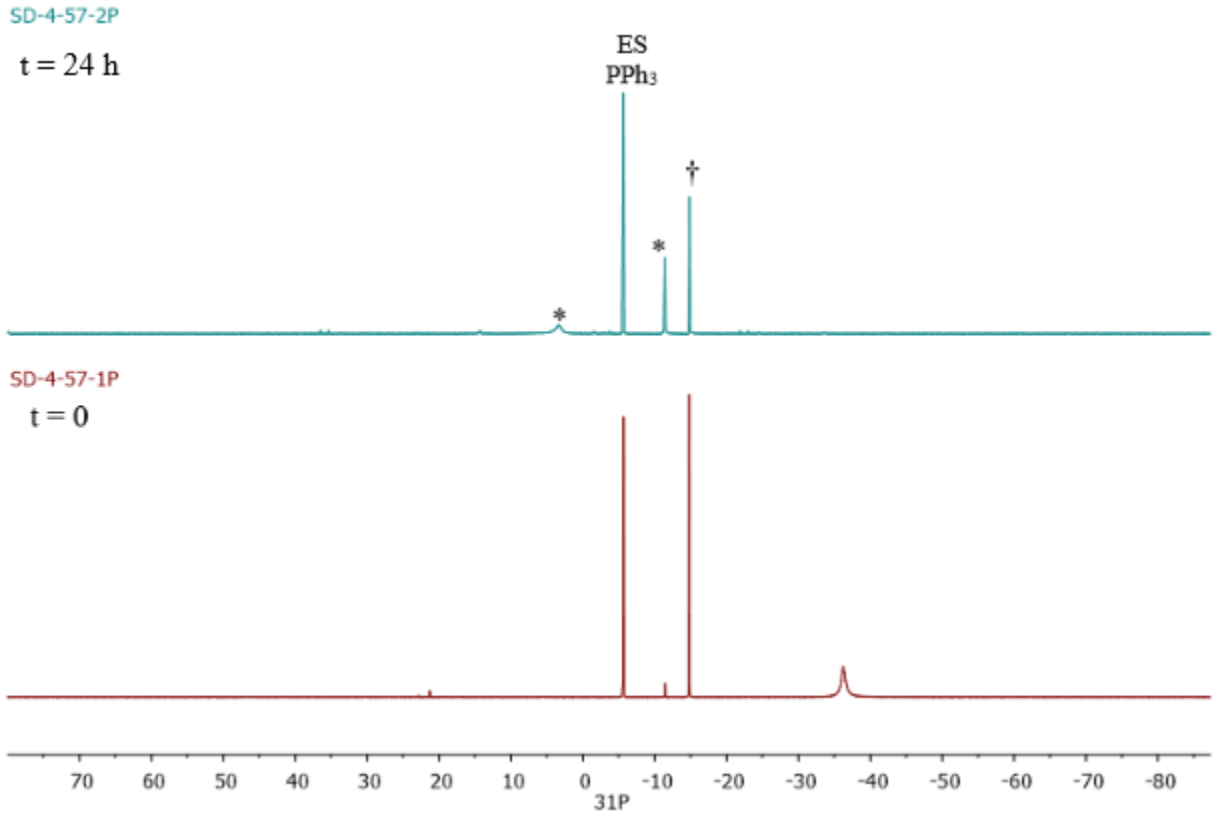
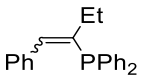


Figure S.71. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of phenylacetylene
Eqn (4) and Table S3

Prepared in accordance with the general procedure with one equiv. of diphenylphosphine. 41% conversion of phenylacetylene was measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy after 24 h of 360 nm irradiation. Spectra is in accordance with previous reports.[21]

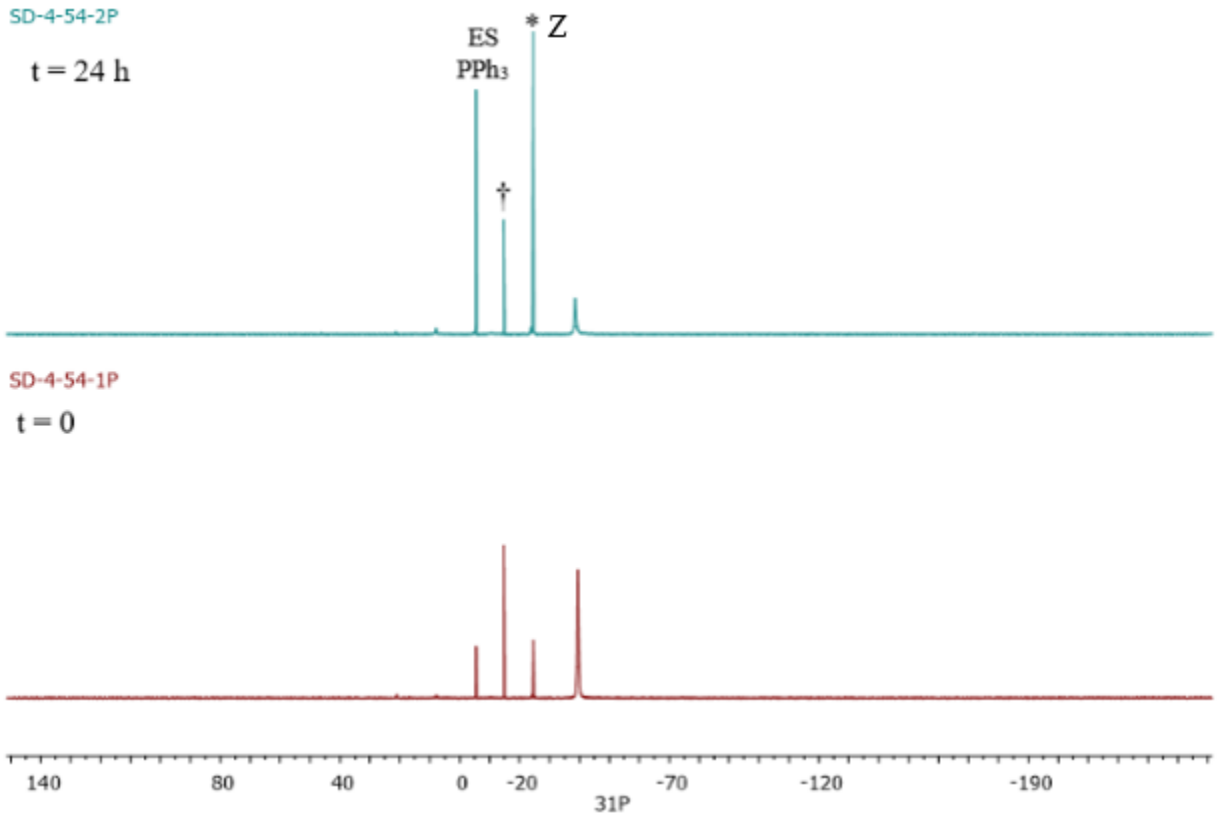
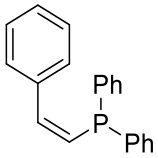


Figure S.72. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of phenylacetylene with one equiv. of diphenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

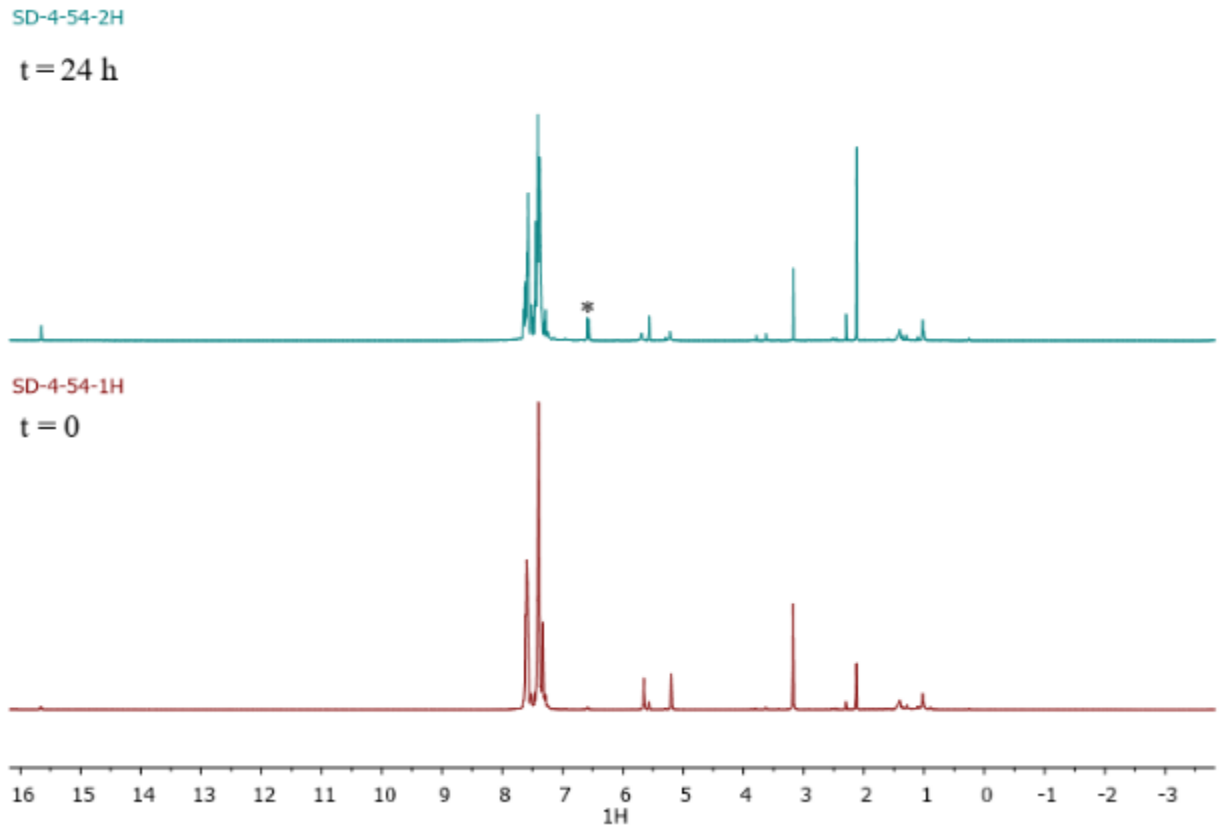
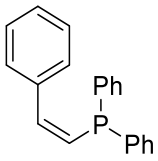


Figure S.73. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz) at t = 24 h of 360 nm irradiation



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 3-hexyne
Table S3

Prepared according to the general procedure with two equiv. of phenylphosphine and an external standard of PPh_3 added. 71% of 3-hexyne was converted after 24 h of 360 nm irradiation with 1:1.5 *Z:E* selectivity as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[4]

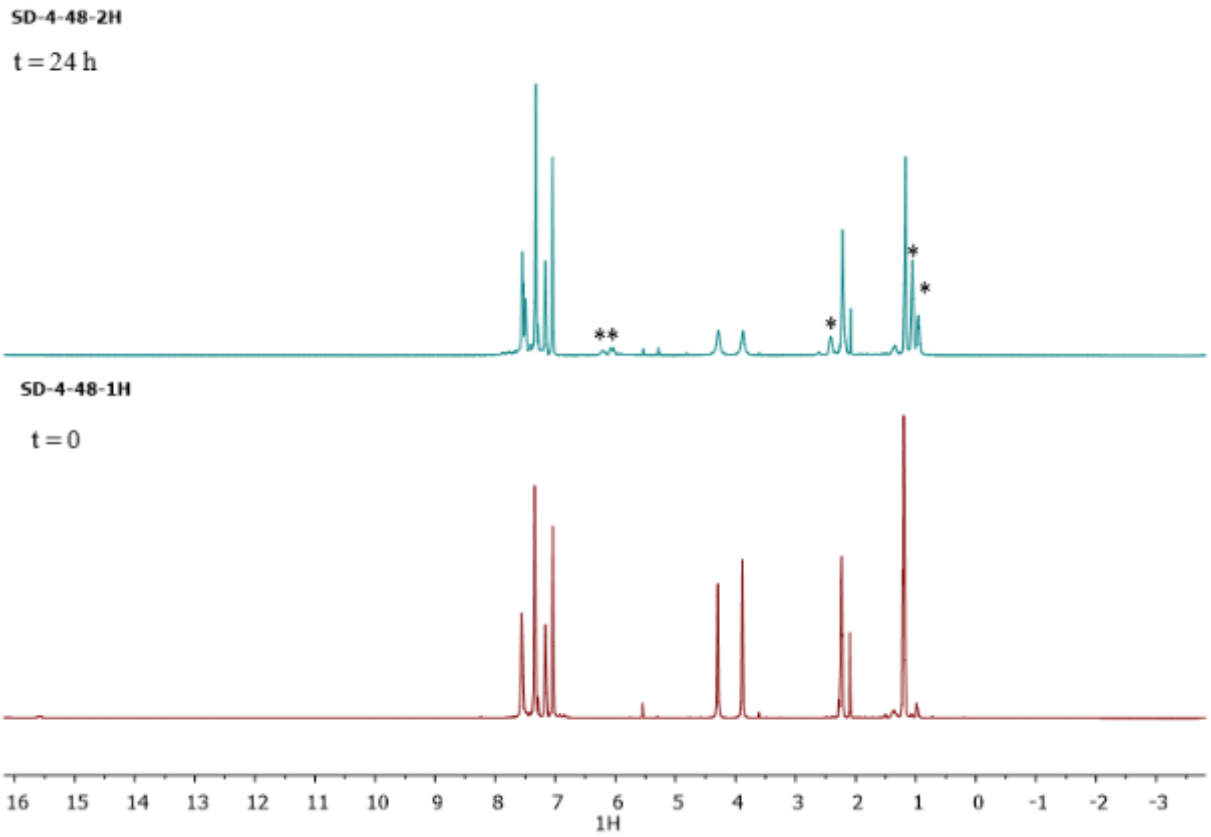
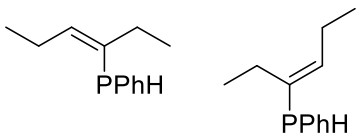


Figure S.74. Stacked ^{1}H NMR spectra ($CDCl_3$, 500 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of 3-hexyne with one equiv. of phenylphosphine by 5 mol % of **1** under 360 nm irradiation (continued)

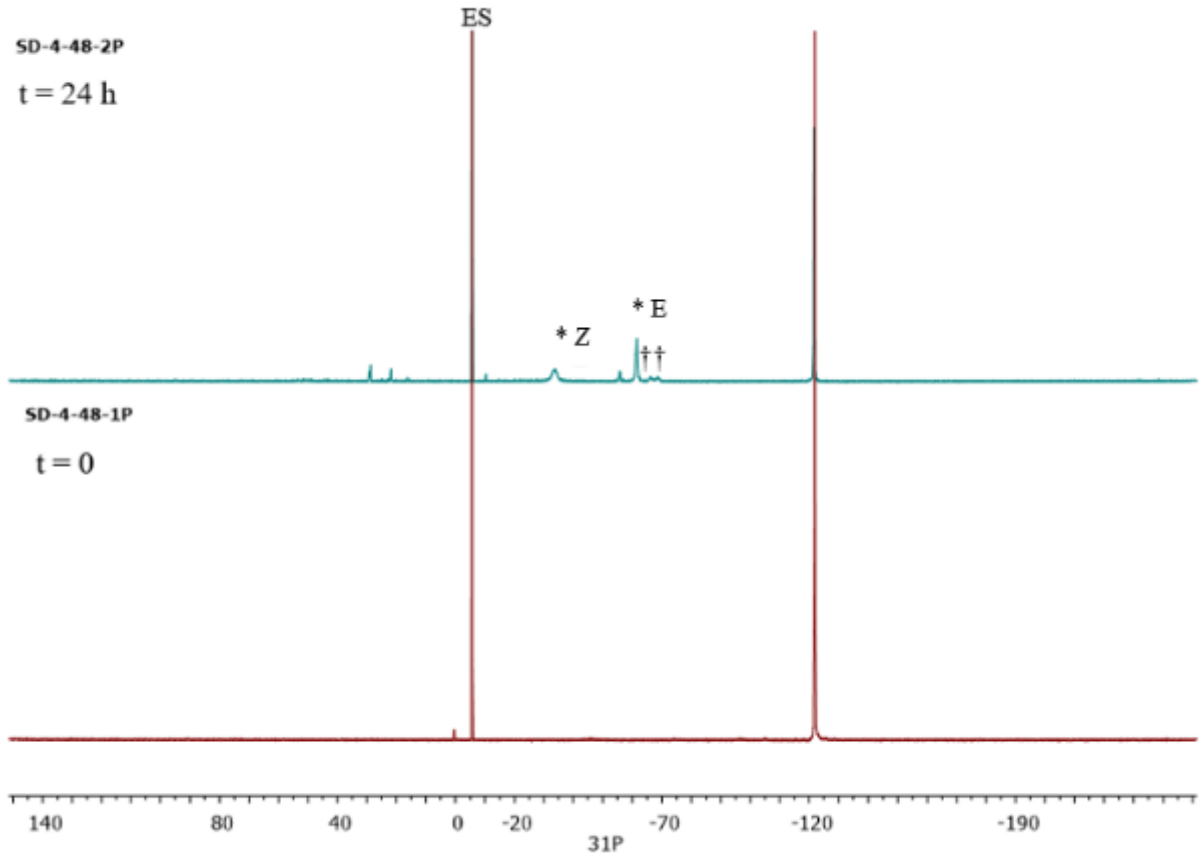
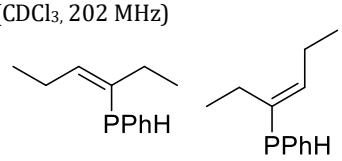


Figure S.75. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of diphenylacetylene
Table S3

Prepared according to general procedure with two equiv. of phenylphosphine and an external standard of PPh_3. 58% of diphenylacetylene was converted after 24 h of 360 nm irradiation with 2.1:1 *Z:E* selectivity as measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy. Spectra are consistent with previous reports.[25]

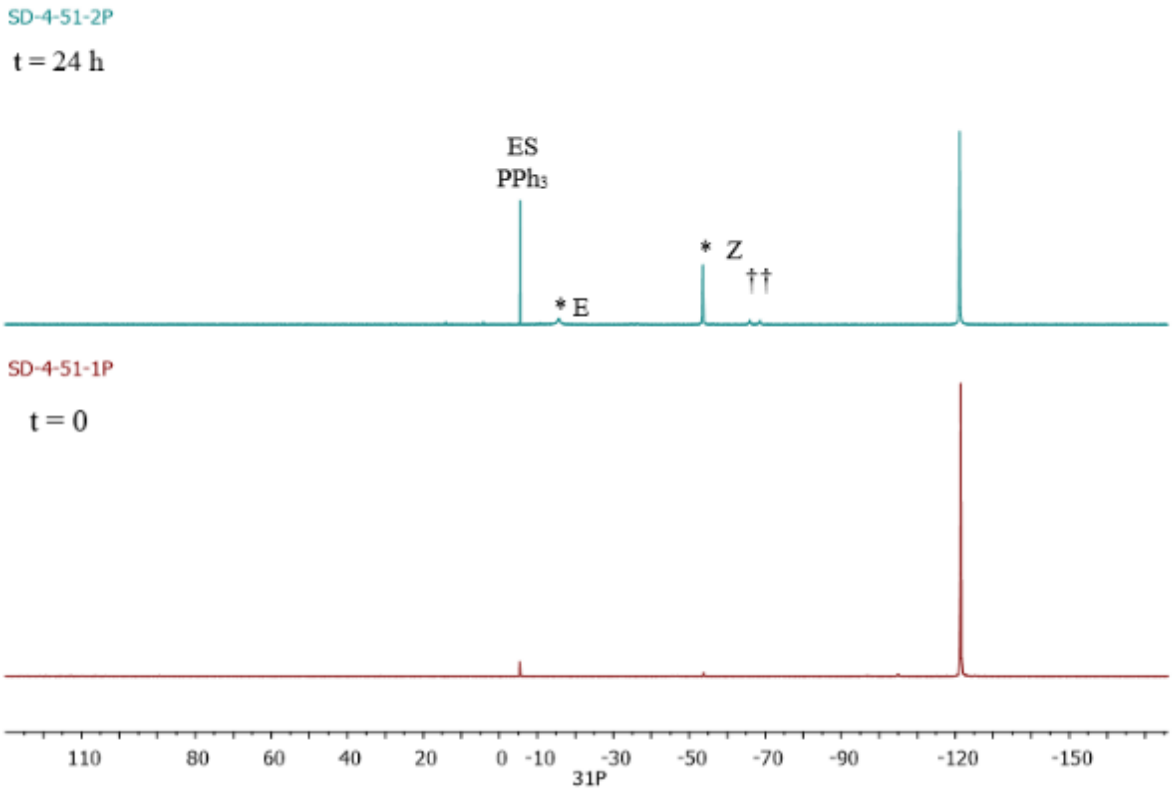
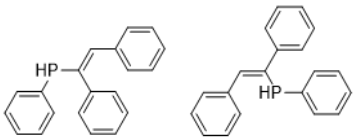


Figure S.76. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of phenylacetylene with two equiv. of phenylphosphine
Table S3

Prepared by the general procedure with two equiv. of phenylphosphine and an external standard of PPh_3. 88% of phenylacetylene was converted to the double P-H activation product after 24 h of 360 nm irradiation with 2.7:1 Z,Z:E,Z selectivity as measured by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. Z,Z is isomer is consistent with the literature.[26] The E:Z isomer has not been characterized by NMR spectroscopy for this compound but has been for several para substituted phenylacetylenes derivatives and our assignment.

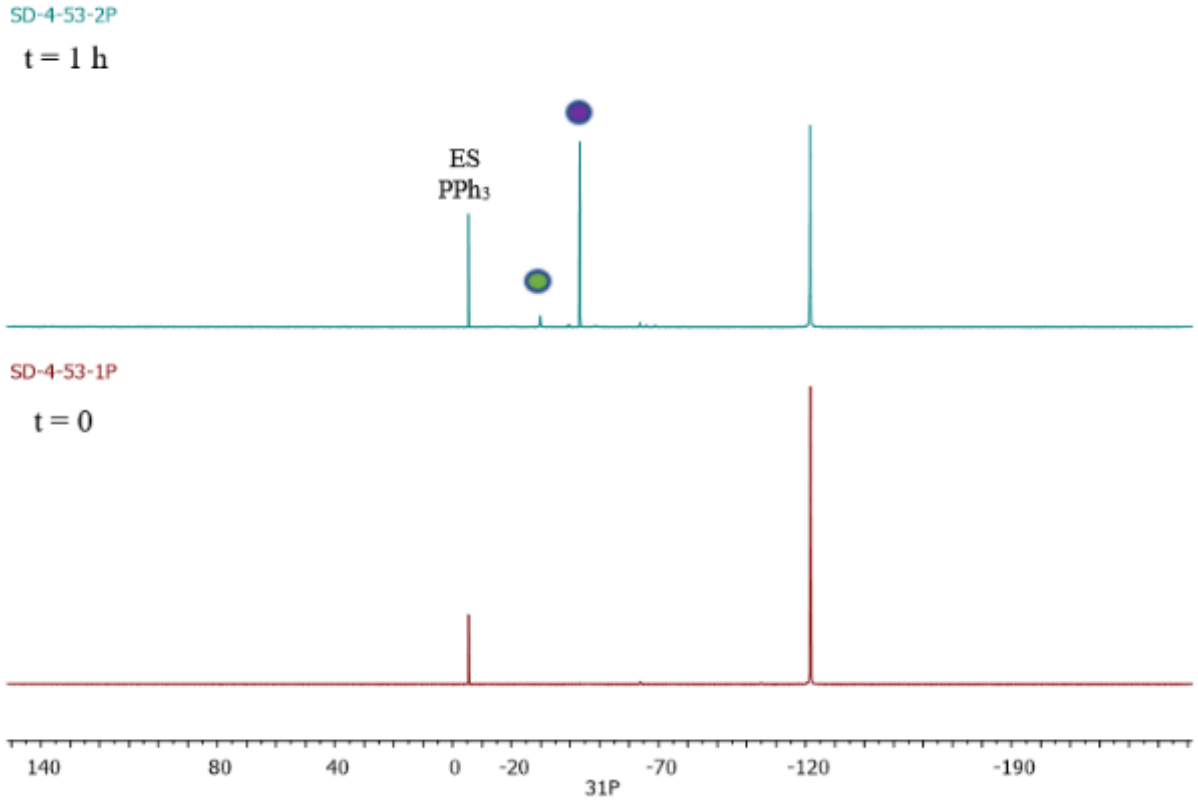
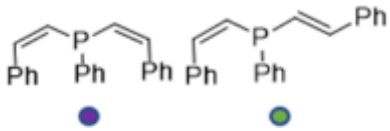


Figure S.77. Stacked $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$, 202 MHz)



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Hydrophosphination of diphenylacetylene with two equiv. of diphenylphosphine by **1**
Table S3

Prepared in accordance with the general procedure with two equiv. of diphenylphosphine. 36% conversion of diphenylacetylene with 35:1 *Z:E* selectivity was measured by ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy after 72 h 360 nm irradiation. Spectra are in accordance with previous reports.[21]

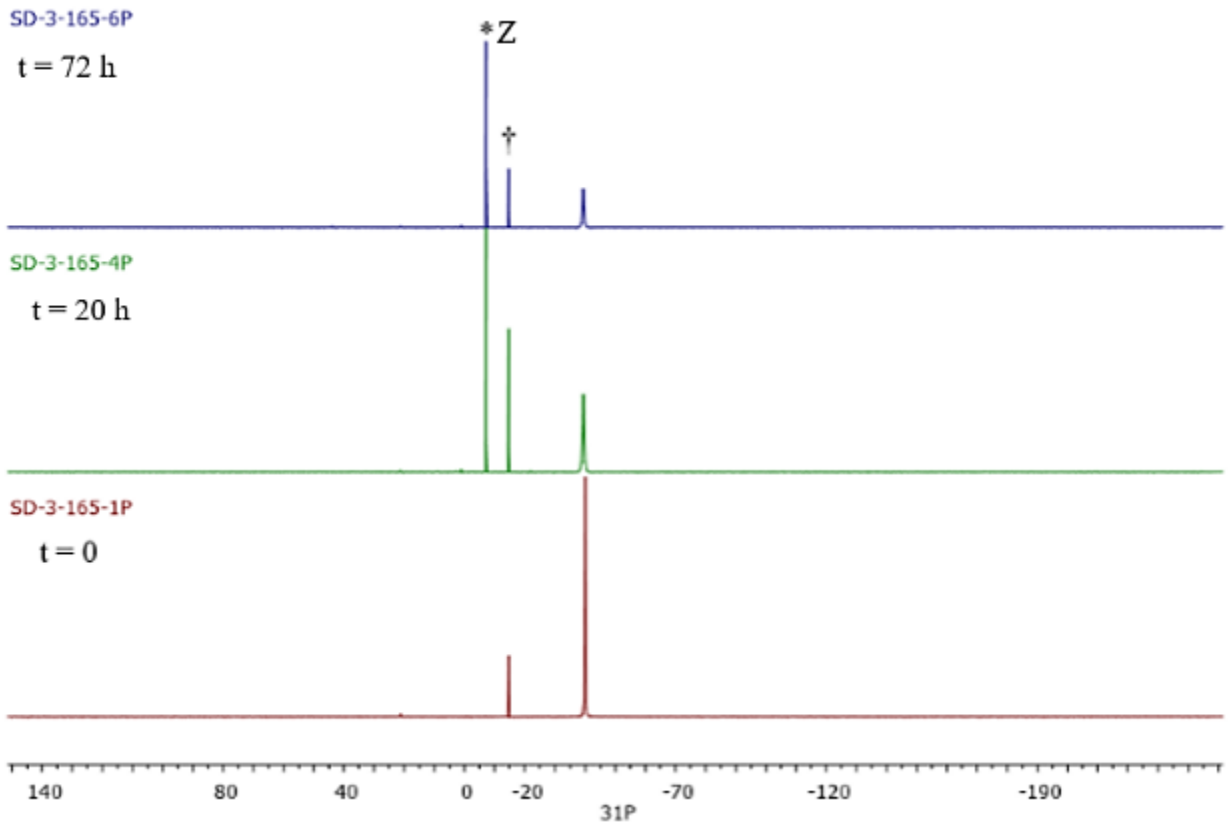
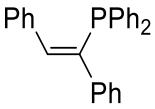


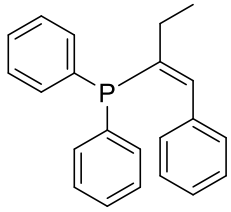
Figure S.78. Stacked $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz)



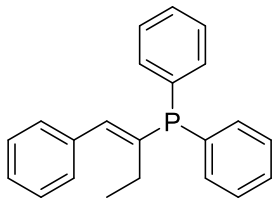
* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (E,Z)-diphenyl(1-phenylbut-1-en-2-yl)phosphine
Hydrophosphination products of 1-phenyl-1-butyne and diphenylphosphine

Synthesized following the general procedure with one equiv. of diphenylphosphine and the modification that the reaction was scaled up and replicated with 0.99 mg (0.76 mmol) 1-phenyl-1-butyne, 140 mg (0.76 mmol) of diphenylphosphine, 10 mg **1** in 1 ml of $CDCl_3$. Purification of the crude product was achieved by flash column chromatography on silica gel with a 3:1 hexanes: DCM liquid phase. $^{31}P\{^1H\}$ NMR spectroscopy indicated that the product was isolated in earlier fractions as a mixture of isomers and later fractions as the pure Z isomer. Over time, slow oxidation of the products occurred. The Z isomer peaks were determined by subtracting the signal for the previously characterized Z isomer phosphine oxide[27] from the ^1H, ^{13}C, ^{31}P, $^{31}P\{^1H\}$ NMR spectra of later fractions. Assignments were verified by ^{31}P HMBC. The E isomer peaks were determined by subtracting the Z isomer phosphine oxide and phosphine peaks from earlier fractions. The exact splitting patterns for the aromatic region of the products was hampered by overlap of peaks.



(Z)-diphenyl(1-phenylbut-1-en-2-yl)phosphine. ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.29 (15H, Ar), 7.28 – 7.23 (m, 1H), 2.17 – 2.05 (qt, J = 7.3, 1.95 Hz, 2H), 0.99 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.98 (d, $J_{C\text{-}P}$ = 29.2 Hz), 139.27 (d, $J_{C\text{-}P}$ = 21.6 Hz), 137.67 (d, $J_{C\text{-}P}$ = 7.4 Hz), 136.96 (d, $J_{C\text{-}P}$ = 12.4 Hz), 133.32 (d, $J_{C\text{-}P}$ = 18.7 Hz), 129.47 (d, $J_{C\text{-}P}$ = 7.1 Hz), 128.32 (d, $J_{C\text{-}P}$ = 6.2 Hz), 128.24 (s), 127.79 (s), 127.22 (s), 28.97 (d, $J_{C\text{-}P}$ = 4.0 Hz), 13.54 (s). $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ -11.61 (s). MS calcd for $C_{22}H_{22}P$: 317.15 $[M+H]^+$, found: 317.2.



(E)-diphenyl(1-phenylbut-1-en-2-yl)phosphine. ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.24 (Ar), 6.42 (d, J = 10.3 Hz, 1H), 2.51 (dq, J = 14.9, 7.5 Hz, 2H), 1.14 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) unable to clearly assign peaks due to oxide impurity. $^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$) δ 1.11 (s). MS calcd for $C_{22}H_{22}P$: 317.15 $[M+H]^+$, found: 317.2.

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = $Ph_2P\text{-}PPh_2$ or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (E,Z)-diphenyl(1-phenylbut-1-en-2-yl)phosphine (continued)

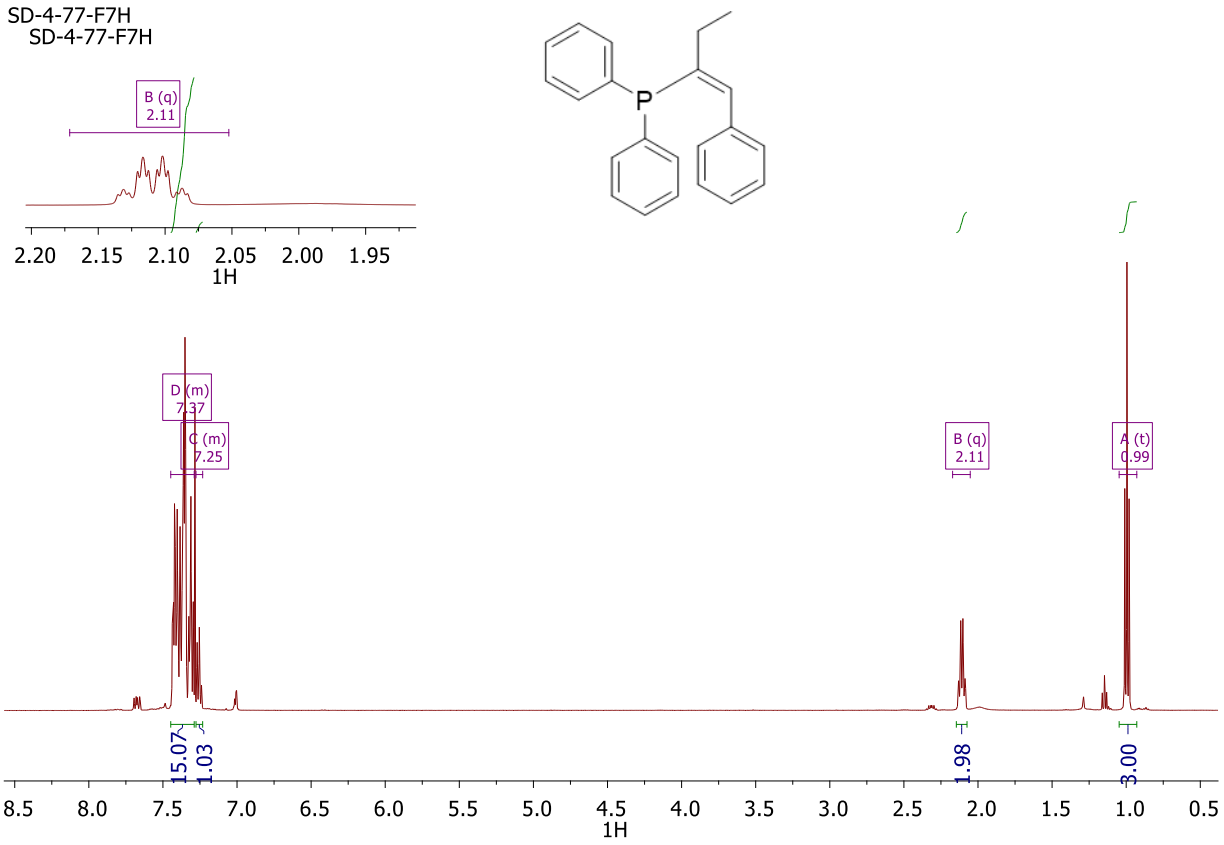


Figure S.79. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (E,Z)-diphenyl(1-phenylbut-1-en-2-yl)phosphine (continued)

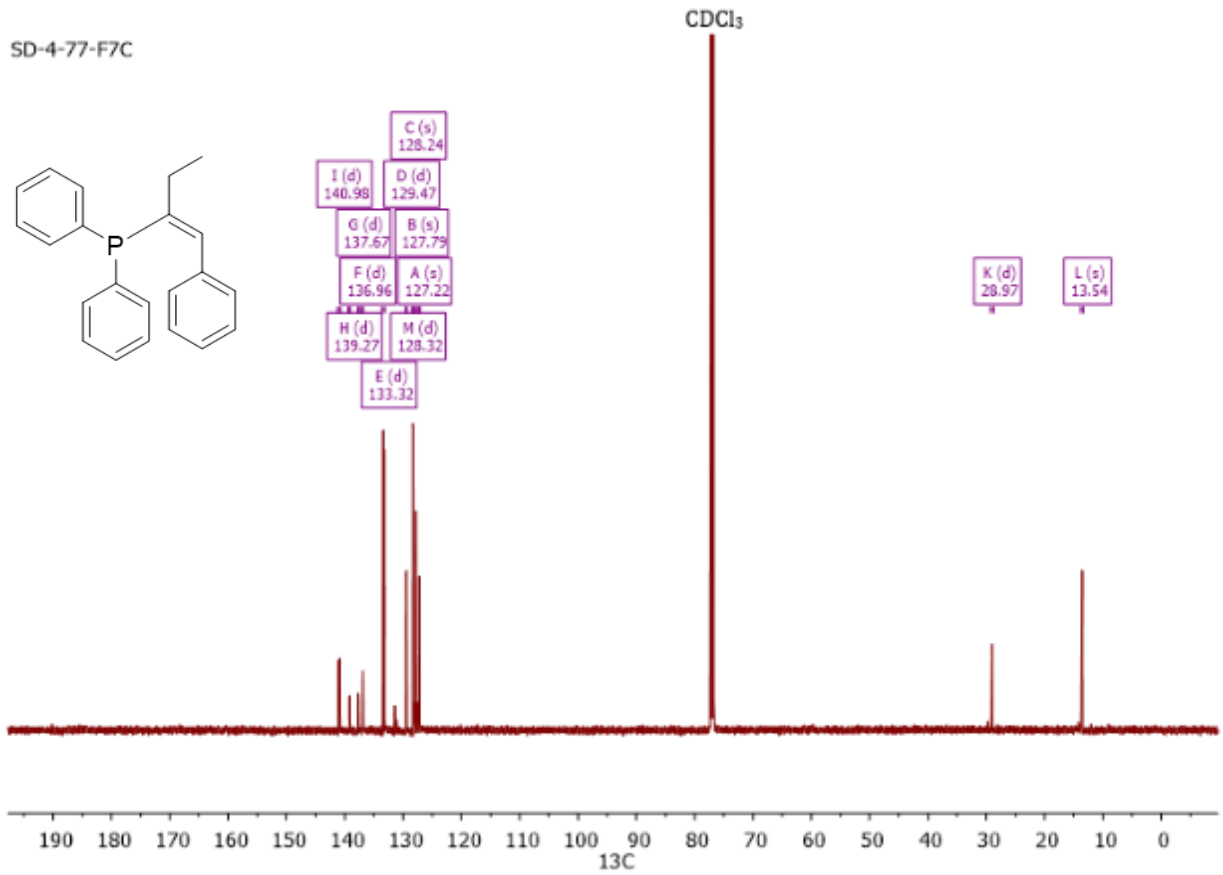


Figure S.80. ^{13}C NMR spectrum ($CDCl_3$, 125 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (E,Z)-diphenyl(1-phenylbut-1-en-2-yl)phosphine (continued)

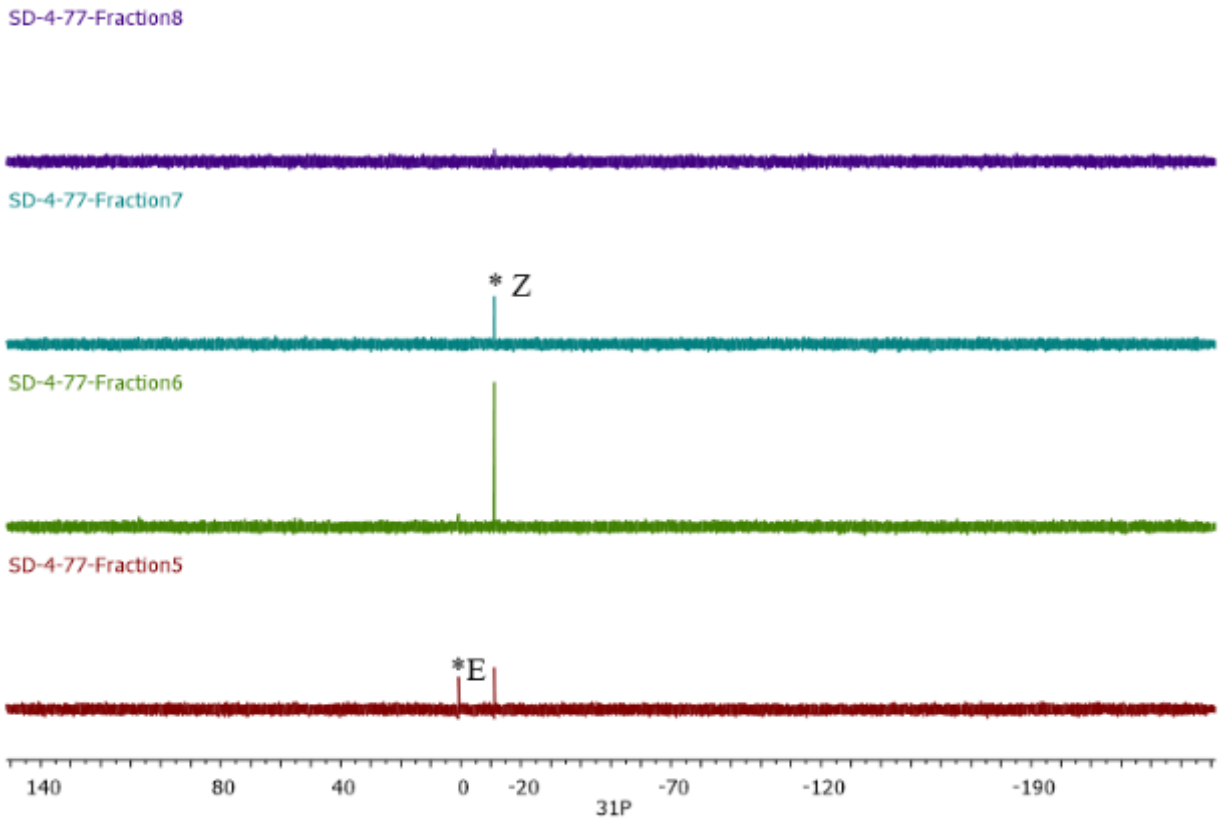
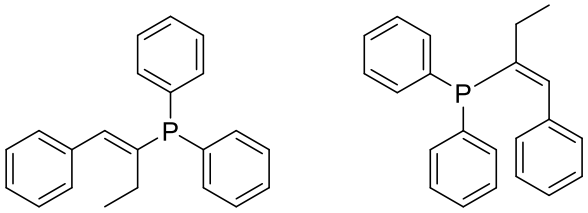


Figure S.81. $^{31}P\{^{1}H\}$ NMR spectra (hexanes/DCM 3:1, 202 MHz) of four isolated fractions



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (E,Z)-diphenyl(1-phenylbut-1-en-2-yl)phosphine (continued)

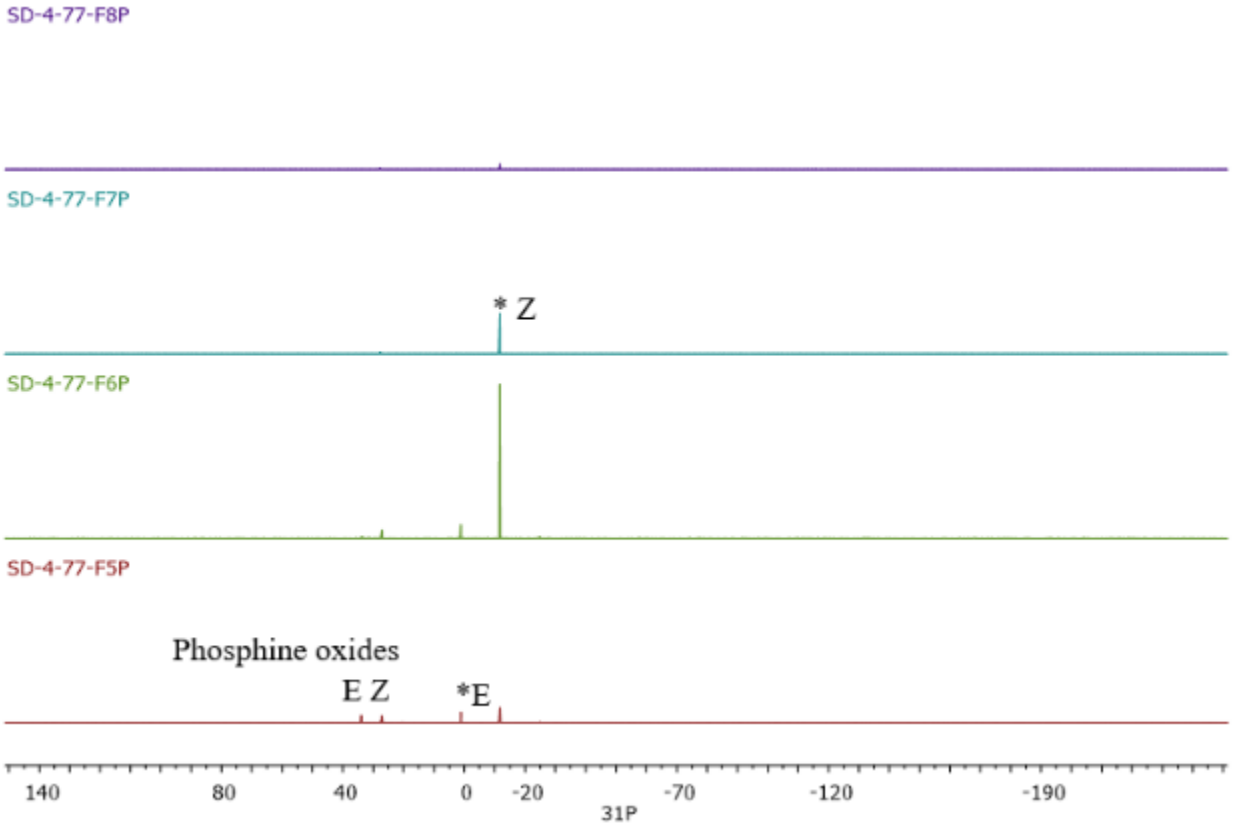
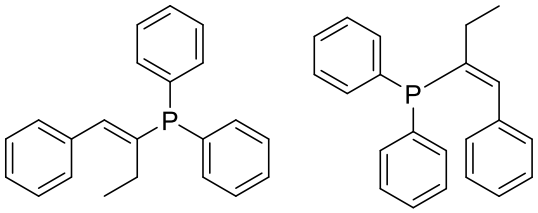


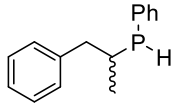
Figure S.82. $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz) of 4 isolated fractions. Some oxidation of the products occurred.



* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (1-phenylprop-2-yl)diphenylphosphine
Hydrophosphination products of β-methyl styrene and phenylphosphine

Synthesized following the general procedure with two equiv. of phenylphosphine. Purification of the crude product was achieved in a dry box by flash column chromatography on silica gel with a 3:1 Hexanes: DCM liquid phase followed by evaporation of volatile materials by vacuum. Fraction 3 contained 25.3 mg (0.11 mmol, 29% yield) of the product in 98% purity by $^{31}P\{^{1}H\}$ NMR spectroscopy. The 2% phosphorus impurity is likely the markovnikov addition product signal. Fractions 4,5, and 6 contained a total of 46.7 mg (za53.8%) of 100% pure product as determined by ^{31}P NMR spectroscopy for a total isolated yield of 82% in 99% purity.



(1-phenylprop-2-yl)diphenylphosphine: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.08 (10H, Ar), 4.11 (ddd, *J* = 211.2, 20.2, 4.9 Hz, 1H), 2.92 (dd, *J* = 12.8, 5.7 Hz, 1H), 2.63 – 2.46 (m, 1H), 2.37 – 2.22 (m, 1H), 1.13 – 0.96 (m, 3H). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) δ -28.65 (s), -32.54 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.64 (s), 135.16 – 134.55 (m), 134.42 (d, *J* = 12.2 Hz), 129.03 (d, *J* = 11.9 Hz), 128.75 – 128.01 (m), 126.09 (s), 42.34 (d, *J* = 9.3 Hz), 41.76 (s), 31.61 (dd, *J* = 24.8, 9.3 Hz), 18.90 (s), 18.12 (d, *J* = 16.3 Hz).^{31}P NMR (202 MHz, $CDCl_3$) δ -27.86 (d, *J* = 212.4 Hz), -31.77 (d, *J* = 211.9 Hz). MS calcd for $C_{15}H_{17}P$: 229.27 $[M+H]^+$, found: 229.3

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (1-phenylprop-2-yl)diphenylphosphine (continued)

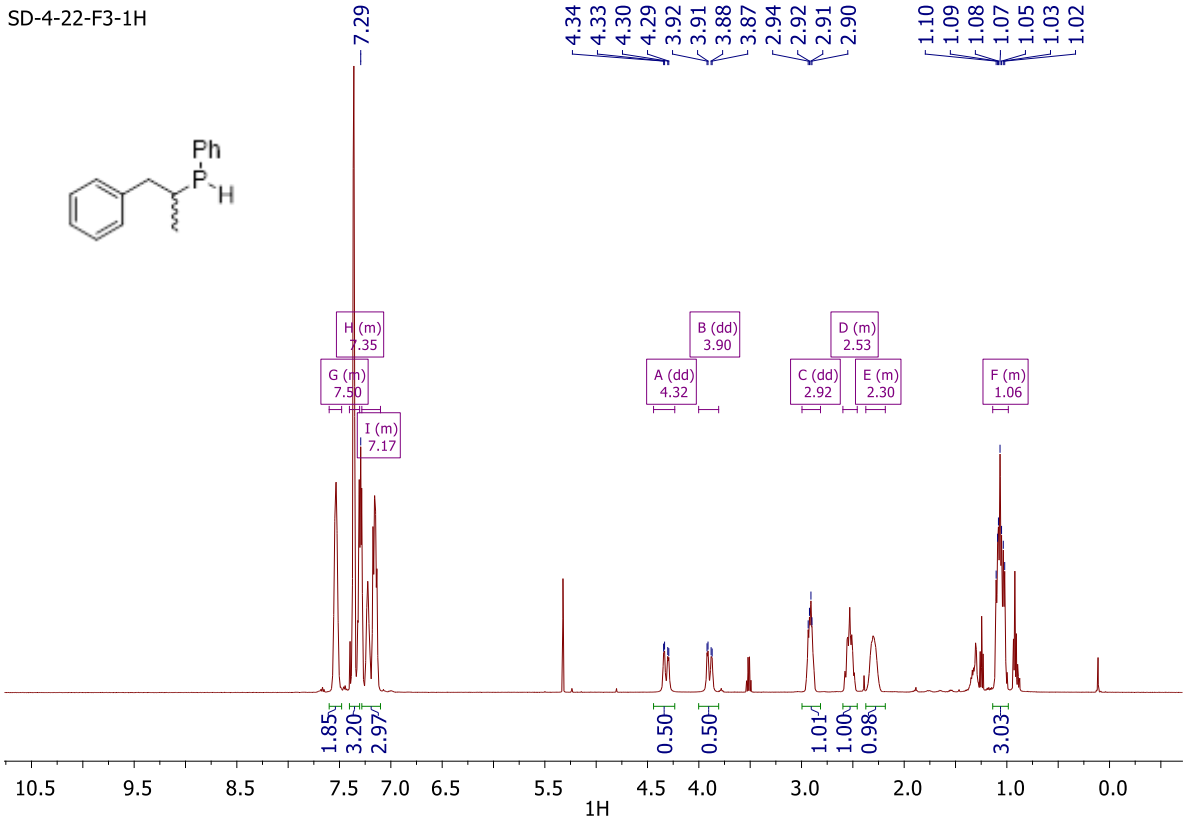


Figure S.83. ^{1}H NMR spectrum ($CDCl_3$, 500 MHz) of (1-phenylprop-2-yl)diphenylphosphine. Residual ammounts of residual solvent (DCM, hexanes) are visible.

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products**:** (1-phenylprop-2-yl)diphenylphosphine (continued)

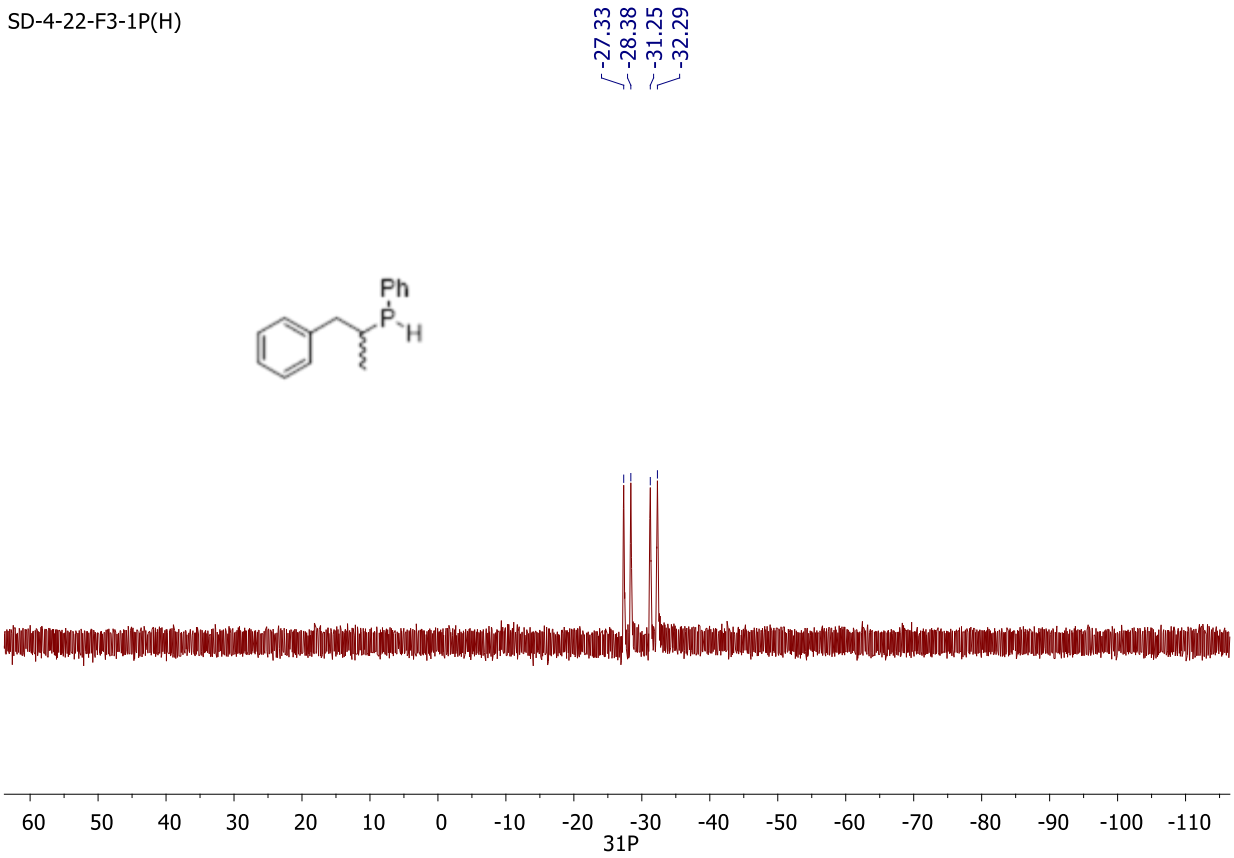


Figure S.84. ^{31}P NMR spectrum ($CDCl_3$, 202 MHz) of (1-phenylprop-2-yl)diphenylphosphine

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (1-phenylprop-2-yl)diphenylphosphine (continued)

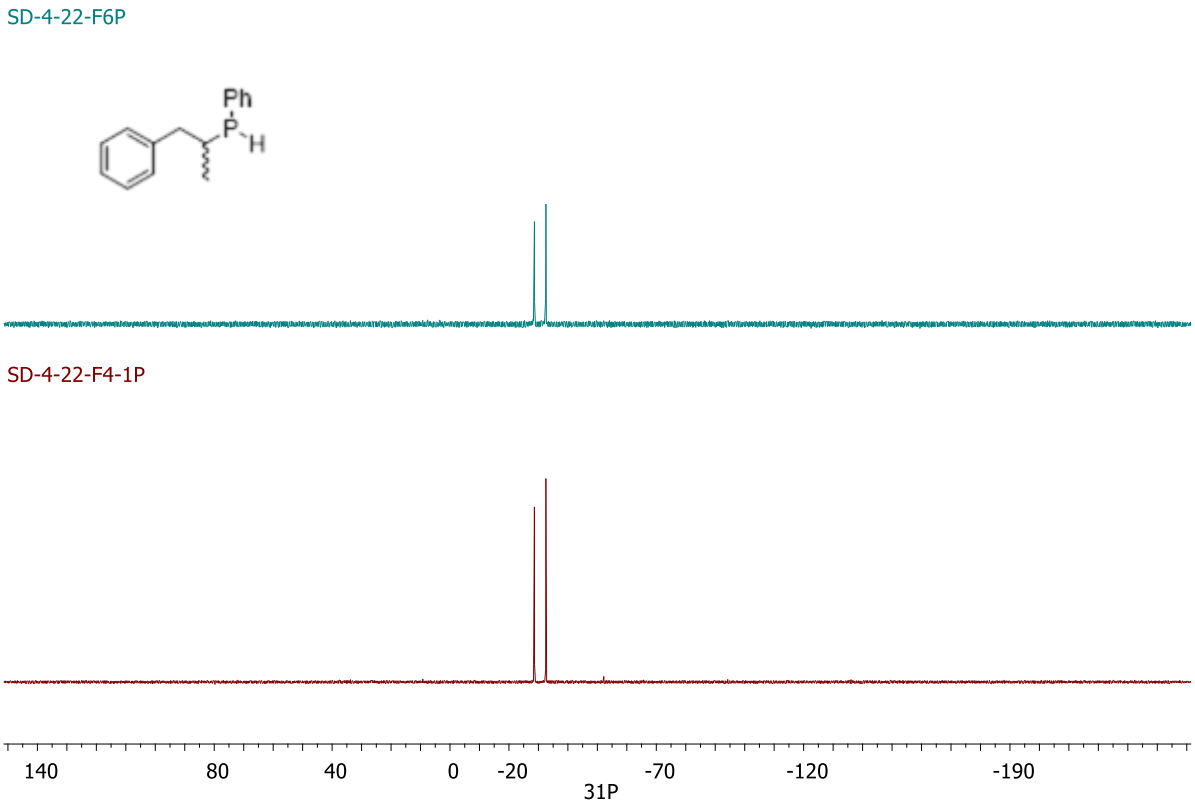


Figure S.85. $^{31}P\{^{1}H\}$ NMR spectra ($CDCl_3$, 202 MHz) of two pure fractions of (1-phenylprop-2-yl)diphenylphosphine

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

Characterization of new products: (1-phenylprop-2-yl)diphenylphosphine (continued)

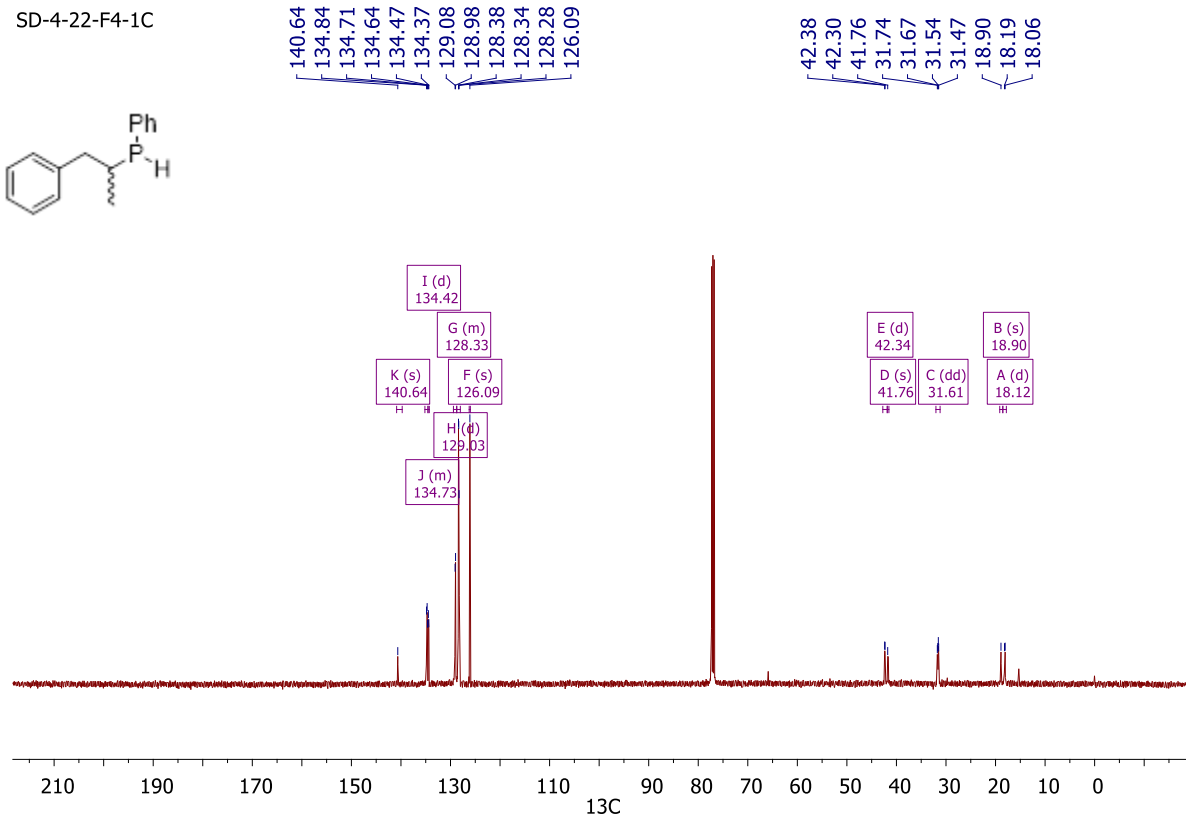


Figure S.86. ^{13}C NMR spectra ($CDCl_3$, 126 MHz)

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane

References

1. H. Gulyás, J. Benet-Buchholz, E. C. Escudero-Adan, Z. Freixa and P. W. N. M. van Leeuwen, *Chem. - Eur. J.*, 2007, **13**, 3424.
2. I. Paterson, S. J. Fink, L. Y. W. Lee, S. J. Atkinson and S. B. Blakey, *Org. Lett.*, 2013, **15**, 3118.
3. B. J. Ackley, J. K. Pagano and R. Waterman, *Chem. Commun.*, 2018, **54**, 2774.
4. C. A. Bange and R. Waterman, *ACS Catal.*, 2016, **6**, 6413.
5. C. A. Bange, M. A. Conger, B. T. Novas, E. R. Young, M. D. Liptak and R. Waterman, *ACS Catal.*, 2018, **8**, 6230.
6. M. B. Ghebreab, C. A. Bange and R. Waterman, *J. Am. Chem. Soc.*, 2014, **136**, 9240.
7. M. D. Gordon and L. D. Quin, *J. Am. Chem. Soc.*, 1976, **98**, 15.
8. A. K. King, A. Buchard, M. F. Mahon and R. L. Webster, *Chem. - Eur. J.*, 2015, **21**, 15960.
9. R. Waterman, *Organometallics*, 2007, **26**, 2492.
10. D. G. Yakhvarov, Y. S. Ganushevich and O. G. Sinyashin, *Mendeleev Commun.*, 2007, **17**, 197.
11. A. K. King, K. J. Gallagher, M. F. Mahon and R. L. Webster, *Chem. - Eur. J.* , 2017, **23**, 9039.
12. A. O. Tolpygin, A. V. Cherkasov, G. K. Fukin, T. A. Kovylina, K. A. Lyssenko and A. A. Trifonov, *Eur. J. Inorg. Chem.*, 2019, **2019**, 4289.
13. N. A. Isley, R. T. Linstadt, E. D. Slack and B. H. Lipshutz, *Dalton Trans.*, 2014, **43**, 13196.
14. M. P. Cibuzar, S. G. Dannenberg and R. Waterman, *Isr. J. Chem.*, 2019, **60**, 446.
15. I. V. Lapshin, O. S. Yurova, I. V. Basalov, V. Y. Rad'kov, E. I. Musina, A. V. Cherkasov, G. K. Fukin, A. A. Karasik and A. A. Trifonov, *Inorg. Chem.*, 2018, **57**, 2942.
16. W. S. Tay, X.-Y. Yang, Y. Li, S. A. Pullarkat and P.-H. Leung, *Dalton Trans.*, 2019, **48**, 4602.
17. R. G. Belli, K. M. E. Burton, S. A. Rufh, R. McDonald and L. Rosenberg, *Organometallics*, 2015, **34**, 5637.
18. L. Routaboul, F. Toulgoat, J. Gatignol, J.-F. Lohier, B. Norah, O. Delacroix, C. Alayrac, M. Taillefer and A.-C. Gaumont, *Chem. - Eur. J.*, 2013, **19**, 8760.
19. A. K. King, K. J. Gallagher, M. F. Mahon and R. L. Webster, *Chem. - Eur. J.*, 2017, **23**, 9039.
20. T. H. Lemmen, G. V. Goeden, J. C. Huffman, R. L. Geerts and K. G. Caulton, *Inorg. Chem.*, 1990, **29**, 3680.
21. B. T. Novas, C. A. Bange and R. Waterman, *Eur. J. Inorg. Chem.*, 2019, **2019**, 1640.
22. G. Phillips, S. Hermans, J. R. Adams and B. F. G. Johnson, *Inorganica Chim. Acta*, 2003, **352**, 110.
23. H. Schmidt, *J. Prakt. Chem.*, 1997, **339**, 482.
24. M. M. I. Basiouny, D. A. Dollard and J. A. R. Schmidt, *ACS Catal.*, 2019, **9**, 7143.
25. G. Zhao, F. Basuli, U. J. Kilgore, H. Fan, H. Aneetha, J. C. Huffman, G. Wu and D. J. Mindiola, *J. Am. Chem. Soc.*, 2006, **128**, 13575.
26. N. T. Coles, M. F. Mahon and R. L. Webster, *Chem. Commun.*, 2018, **54**, 10443.
27. H. Wang, Y. Li, Z. Tang, S. Wang, H. Zhang, H. Cong and A. Lei, *ACS Catal.*, 2018, **8**, 10599.

* = hydrophosphination product, ** = double addition hydrophosphination product, † or †† = Ph_2P-PPh_2 or PhPH-PhPH, ǂ = acetylacetone, ES = PPh_3 external standard, TMB = 1,3,5-trimethoxy benzene, TMS = tetramethyl silane