

Mapping Catalyst Activation, Turnover Speciation and Deactivation in Rh/PPh₃-catalysed Olefin hydroformylation

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Supplementary information

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1. Experimental

1.1 Materials and methods

Unless stated otherwise, all manipulations were carried out under an inert atmosphere of dry argon using standard Schlenk line techniques. 1-hexene was purchased from Acros Organics, stirred over potassium overnight followed by a fractional distillation under argon over the same metal. Triphenylphosphine, triphenylphosphate, $[\text{Rh}(\text{acac})(\text{CO})_2]$, $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$, $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$, $[\text{Rh}(\text{acac})_3]$, $[\text{Rh}_4\text{CO}_{12}]$ and 1,3,5-trimethoxybenzene were purchased in the highest purity available and used without further purification. Toluene was freshly distilled from sodium under argon before use. Carbon monoxide (99.99 %) and hydrogen (99.95 %) gases were supplied by BOC UK Ltd.

The hydroformylation of 1-hexene was carried out in a Büchi Miniclave pressure reactor made of glass with a stainless-steel lid connected to the FlowNMR apparatus via 1/16" Swagelok connections. A micro-annular gear pump (mzr-6355 from HNP Mikrosysteme GmbH) was used to circulate the reaction mixture through the 1/16" polyetheretherketone (PEEK, Upchurch Scientific) tubing with 0.76 mm i.d. connected to an InsightMR flow tube (Bruker) placed in the probe of the spectrometer. The inner volume the entire flow system was approximately 6.4 mL.

Static NMR experiments (not using the FlowNMR apparatus) that needed an atmosphere of CO and/or H₂, were carried out in pressure valved NMR tubes S-5-500-IPV-7, S-5-500-MW-IPV-7 and S-5-500—HW-IPV-7 from Norell rated to 6, 9 and 12 bar, respectively.

NMR spectra were recorded on a Bruker 500 MHz Advance II⁺ Ultrashield equipped with a nitrogen-cooled BBO Prodigy CryoProbe. ¹H NMR chemical shifts are referenced against TMS (99.5 % purity in CDCl₃) and ³¹P NMR shifts are referenced to 85 % H₃PO₄. The reaction monitoring software used was InsightMR, and data processing was performed with TopSpin 4.0.6 and DynamicCenter 2.5.6.

Single crystal X-ray diffraction analysis was carried out by Dr Gabriele Kociok-Köhn from the Material and Chemical Characterisation Facility at the University of Bath using a RIGAKU

SuperNova Dual EoS2 single crystal diffractometer with micro-focused Cu-K α ($\lambda = 1.54184 \text{ \AA}$) radiation. Diffractograms were collected at 150K, and unit cell determination, data reduction and absorption correction were performed using the CrysAlisPro software. Structures were solved by direct methods and refined by a full-matrix least-squares procedure based on F^2 . Hydrogen atoms were included in ideal positions and refined using a riding model.

1.1 Procedure for Rh-hydroformylation of 1-hexene studied by operando FlowNMR

Caution: carbon monoxide is a colourless, odourless, flammable and highly toxic gas – experiments should only be conducted in the presence of a calibrated CO sensor.

The FlowNMR apparatus was flushed with laboratory grade toluene and then purged with argon for at least 10 minutes to remove traces of air and moisture. Triphenylphosphine (see table below), dicarbonyl(acetylacetonato)rhodium(I) (12.90 mg, 0.05 mmol), 1,3,5-trimethoxybenzene (33.64 mg, 2 mmol) and triphenylphosphate (73.09 mg, 0.22 mmol) were added to the pressure glass vessel together with a teflon-coated stir bar followed by sealing of the autoclave with all tubing attached. The system was leak-checked, vacuum-argon cycled three times at room temperature and then kept under argon. The inlet of the flow tube was then moved into a separate Schlenk flask that contained dry toluene under argon, and the outlet to the waste bottle. Dry toluene was then pumped through the flow tube for 5 minutes to leave the transfer lines, pump and flow tube filled with dry solvent (6.4 mL). Thereafter, both flow tube ends were reconnected to the reactor which was topped up with dry toluene (15 mL) and 1-hexene (84.16 mg, 1.25 mL, 10 mmol) against a flow of argon. The FlowNMR tube and tip were then inserted manually into the spectrometer, stirring started and the reaction mixture was pumped through the system at 4 mL/min once all solids had fully dissolved. The reactor, heat exchanger and NMR probe were heated to 50 °C (isothermal experiments) or to the desired temperature (50 °C, 10 °C and 0 °C respectively for controlled temperature gradients), and once the temperature had stabilised throughout the system the NMR spectrometer lock was turned off, shimmed on ^1H peaks and tuned to proton and phosphorus. Spectra of the reagents were recorded both statically and at 4 mL/min. Acquisition parameters for interleaved ^1H , selectively excited ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR measurements were entered (details below) and the sequence commenced to start the FlowNMR reaction monitoring. After acquisition of at least one sequence of measurements the autoclave was firstly pressurised with 5 bar H_2 followed by 5 bar of CO to start the reaction. At the end of the reaction additional calibration spectra with and without flow were recorded before all heating was switched off, the flow stopped, and the reactor carefully vented into the fumehood.

Table S1. Amounts of PPh₃ charged within the autoclave reactor for each flow run reaction with different number of ligand equivalents.

	PPh ₃ loadings
[PPh ₃]/[Rh] = 0	-
[PPh ₃]/[Rh] = 1	13.12 mg, 0.05 mmol
[PPh ₃]/[Rh] = 3	39.35 mg, 0.15 mmol
[PPh ₃]/[Rh] = 6	78.69 mg, 0.3 mmol
[PPh ₃]/[Rh] = 10	131.15 mg, 0.5 mmol
[PPh ₃]/[Rh] = 20	262.30 mg, 1 mmol
[PPh ₃]/[Rh] = 100	1311.5 mg, 5 mmol

1.2 Procedure for the activation of Rh precursor under CO and/or H₂ studied by operando FlowNMR

Caution: carbon monoxide is a colourless, odourless, flammable and highly toxic gas – experiments should only be conducted in the presence of a calibrated CO sensor.

The FlowNMR apparatus was flushed with laboratory grade toluene and then purged with argon for at least 10 minutes to remove traces of air and moisture. Triphenylphosphine (see table below), Rh precursor (see table below), 1,3,5-trimethoxybenzene (33.64 mg, 2 mmol) and triphenylphosphate (73.09 mg, 0.20 mmol) were added to the autoclave together with a teflon-coated stir bar followed by sealing of the autoclave with all tubing attached. The system was leak-checked, vacuum-argon cycled three times at room temperature and then kept under argon. The inlet of the flow tube was then moved into a separate Schlenk flask that contained dry toluene under argon, and the outlet to the waste bottle. Dry toluene was then pumped through the flow tube for 5 minutes to leave the transfer lines, pump and flow tube filled with dry solvent (6.4 mL). Thereafter, both flow tube ends were reconnected to the reactor which was topped up with dry toluene (15 mL) against a flow of argon. The FlowNMR tube and tip were then inserted manually into the spectrometer, stirring started and the reaction mixture was pumped through the system at 4 mL/min once all solids had fully dissolved. The reactor (50 °C), heat exchanger (10 °C), and NMR probe (0 °C), were set to the desired temperatures, and once the temperature had stabilised throughout the system the NMR spectrometer lock was turned off, shimmed on ¹H peaks and tuned to proton and phosphorus. Spectra of the reagents were recorded both statically and at 4 mL/min. Acquisition parameters for interleaved ¹H, selectively excited ¹H and ³¹P{¹H} NMR

measurements were entered (details below) and the sequence commenced to start the FlowNMR reaction monitoring. After acquisition of at least one sequence of measurements the autoclave was firstly pressurised with 5 bar H₂ followed by 5 bar of CO to start the reaction. At the end of the reaction additional calibration spectra with and without flow were recorded before all heating was switched off, the flow stopped, and the reactor carefully vented into the fumehood.

Table S2. Amounts of PPh₃ charged within the autoclave reactor for each flow run reaction with different number of ligand equivalents.

	PPh₃ loadings
[PPh₃]/[Rh] = 1	13.12 mg, 0.05 mmol
[PPh₃]/[Rh] = 3	39.35 mg, 0.15 mmol
[PPh₃]/[Rh] = 6	78.69 mg, 0.3 mmol
[PPh₃]/[Rh] = 10	131.15 mg, 0.5 mmol
[PPh₃]/[Rh] = 20	262.30 mg, 1 mmol

Table S3. Rh precursor used for the activation studies by FlowNMR spectroscopy

Rh precursor	Amounts
dicarbonyl(acetylacetonato)rhodium(I) (3)	(12.90 mg, 0.05 mmol)
carbonyltriphenylphosphine(acetylacetonato)rhodium(I) (4)	(24.62 mg, 0.05 mmol)
carbonyl hydrido tris(triphenylphosphine)rhodium(I) (C)	(45.94 mg, 0.05 mmol)
tris(acetylacetonato)rhodium (III) (2)	(20.01 mg, 0.05 mmol)
tetrarhodiumdodecarbonyl (0) (1)	(37.39 mg, 0.05 mmol)

2. Analysis

2.1 FlowNMR acquisition parameters

^1H , selectively excited ^1H , and $^{31}\text{P}\{^1\text{H}\}$ NMR experiments were interleaved in each cycle and continuously executed every 5 minutes until the end of the reaction.

^1H NMR (zg30):

- Number of scans (NS) = 16 s
- Delay (D_1) = 1 s
- Receiver gain (RG) = 9
- Centre of pulse ($O^1\text{P}$) = 4.7 ppm
- Spectral width (SW) = 40 ppm
- Experimental time (Expt) = 42 s

Selective excitation ^1H NMR (seldpfgse_calc.ptg):

- NS = 32 s
- D_1 = 1 s
- RG = 203
- $O^1\text{P}$ = -5 ppm
- SW = 20 ppm
- CNST 21 = -8 ppm
- CNST 55 = 5 ppm
- Expt = 1 min 37 s

$^{31}\text{P}\{^1\text{H}\}$ NMR (zgpg60):

- NS = 320 s
- D_1 = 0.1 s
- RG = 203
- $O^1\text{P}$ = 50 ppm
- SW = 400 ppm
- Expt = 3 min 03 s

Static calibration spectra were recorded with the same parameters but D_1 was changed for every experiment as follows:

- ^1H NMR spectra → D_1 = 60 s
- Selective excitation ^1H NMR spectra → D_1 = 15 s
- $^{31}\text{P}\{^1\text{H}\}$ NMR (zgig60) spectra → D_1 = 90 s

3. Temperature calibration of FlowNMR apparatus

NMR thermometer experiments were performed in two sample NMR tube; one with methanol-d₄ and another with methanol-H₄ to corroborate if the following equations can be applied for both solvents. **Eq. 1** was obtained for deuterated methanol¹ but non-deuterated methanol was used at larger scale in the flow apparatus.

Equation 1. Temperature of NMR probe in function of the distance between the ¹H methyl and OH signals of methanol (in ppm).

$$T = -16.7467 \times shift^2 - 52.130 \times shift + 419.1381$$

The temperature obtained in both samples were virtually identical, indicating that the experiments in the flow system could be carried out with non-deuterated solvent. For the experiments, the four different parts of the flow system; NMR probe, FlowNMR tube, Flow tube and reactor were set at various temperatures. After 15 min of equilibration and methanol-H₄ flowing at 4 mL/min proton experiments were recorded first with automation tuning (ATMA) and then with manual tuning (ATMM) to get 6 spectra of each.

Table S 4. Temperature of the NMR probe calculated by the shift of NMR signals of methanol at different temperatures in parts of the FlowNMR apparatus. ATMA: Automatic tuning and matching, ATMM: Manual tuning and matching.

Reactor at 50 °C, Flow tube at 55 °C, FlowNMR tube at 50 °C, NMR probe at 50 °C

Experiment repetitions	Distance methanol peaks ATMA (ppm)	Distance methanol peaks with ATMM (ppm)		
1	1.53	1.54		
2	1.53	1.54		
3	1.53	1.54		
4	1.53	1.54		
5	1.53	1.54		
6	1.53	1.54		
			T (K) ATMA	T (K) ATMM
average	1.53	1.54	300.4	299.2

Reactor at 50 °C, Flow tube at 55 °C, FlowNMR tube at 55 °C, NMR probe at 50 °C

Experiment repetitions	Distance methanol peaks ATMA (ppm)	Distance methanol peaks ATMM (ppm)		
1	1.39	1.38		
2	1.39	1.38		
3	1.39	1.38		
4	1.39	1.38		
5	1.39	1.38		
6	1.39	1.38		
			T (K) ATMA	T (K) ATMM
average	1.39	1.38	314.4	315.1

Reactor at 50 °C, Flow tube at 60 °C, FlowNMR tube at 60 °C, NMR probe at 50 °C

Experiment repetitions	Distance methanol peaks ATMA (ppm)	Distance methanol peaks ATMM (ppm)		
1	1.36	1.36		
2	1.36	1.36		
3	1.36	1.36		
4	1.36	1.36		
5	1.36	1.36		
6	1.36	1.36		
			T (K) ATMA	T (K) ATMM
average	1.36	1.36	317.2	317.1

Reactor at 50 °C, flow tube at 25 °C, FlowNMR tube at 5 °C, NMR probe at 0 °C

Experiment repetitions	Distance methanol peaks ATMA (ppm)	Distance methanol peaks ATMM (ppm)		
1	1.72	1.72		
2	1.72	1.72		
3	1.72	1.72		
4	1.72	1.72		
5	1.72	1.72		
6	1.72	1.72		
			T (K) ATMA	T (K) ATMM
average	1.72	1.72	279.5	280.0

Reactor at 50 °C, flow tube at 25 °C, FlowNMR tube at 0 °C, NMR probe at 0 °C

Experiment repetitions	Distance methanol peaks ATMA (ppm)	Distance methanol peaks ATMM (ppm)		
1	1.72	1.72		
2	1.72	1.72		
3	1.72	1.72		
4	1.72	1.72		
5	1.72	1.72		
6	1.72	1.72		
			T (K) ATMA	T (K) ATMM
average	1.72	1.72	279.5	280.1

4. Supplementary data

$^{31}\text{P}\{^1\text{H}\}$ NMR

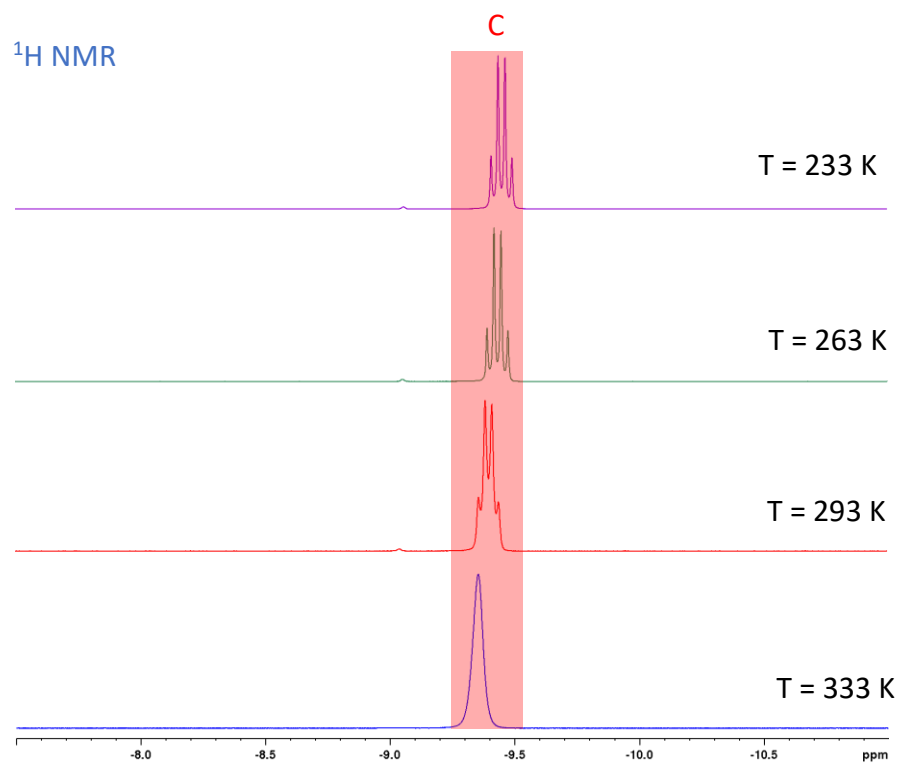
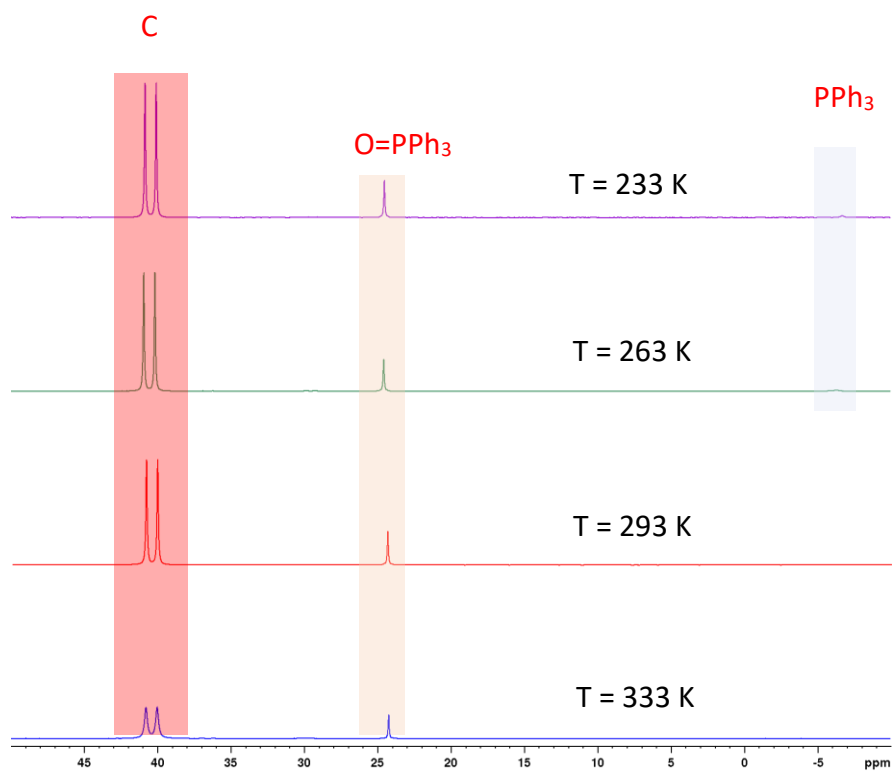
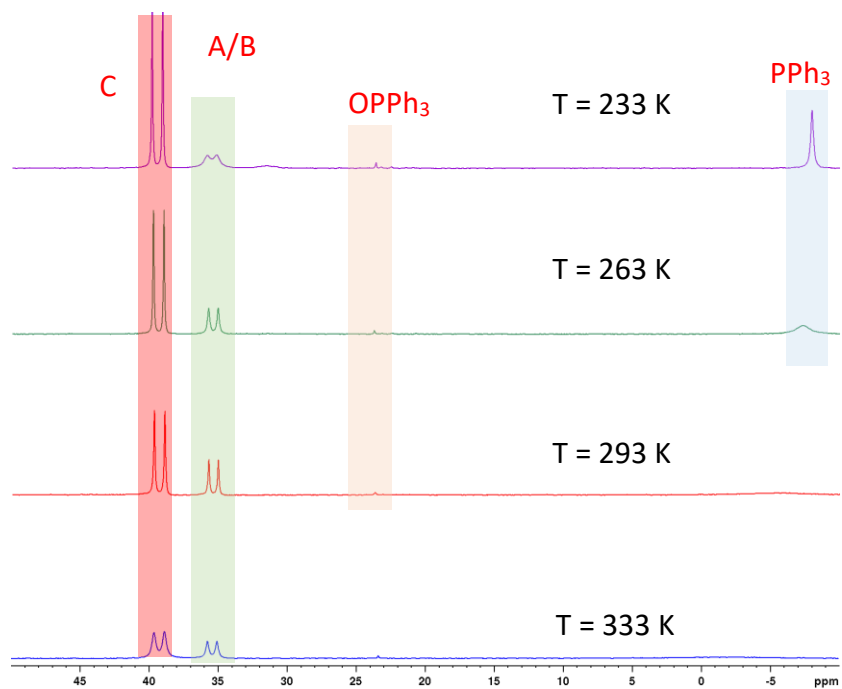


Figure S1. VT $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of the mixture containing 45 mM of $[\text{Rh}(\text{CO})(\text{PPh}_3)_3]$ (C/D), 10 mM of TMB and 10 mM of TPOP in 0.8 mL of non-deuterated toluene under argon.

$^{31}\text{P}\{^1\text{H}\}$ NMR



^1H NMR

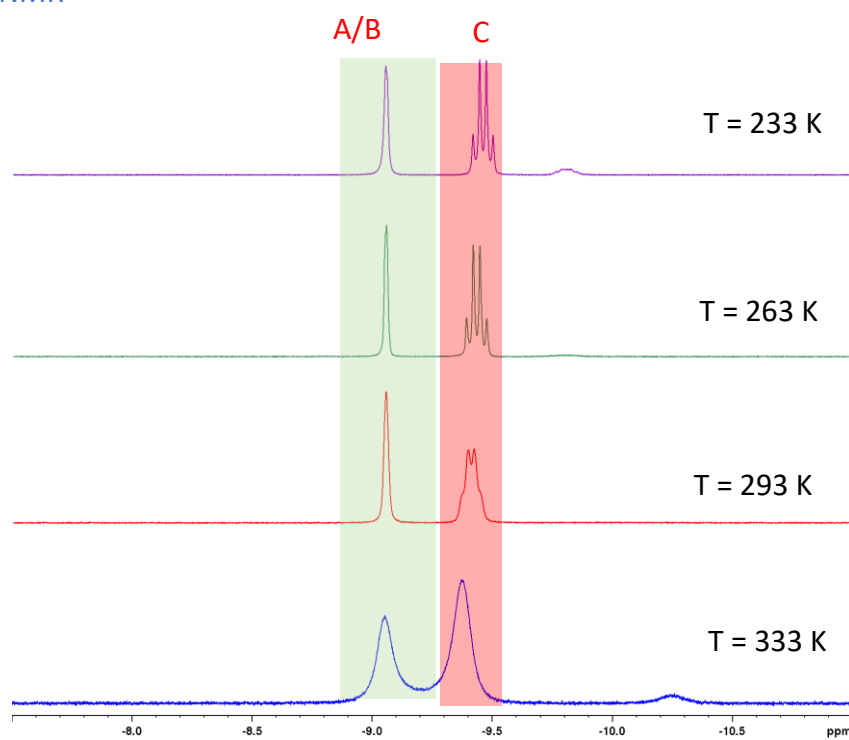


Figure S2. VT $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra of the mixture containing 45 mM of $[\text{RhHCO}(\text{PPh}_3)_3]$ (C/D), 10 mM of TMB and 10 mM of TPOP in 0.8 mL of non-deuterated toluene under 5 bar of H_2 and CO.

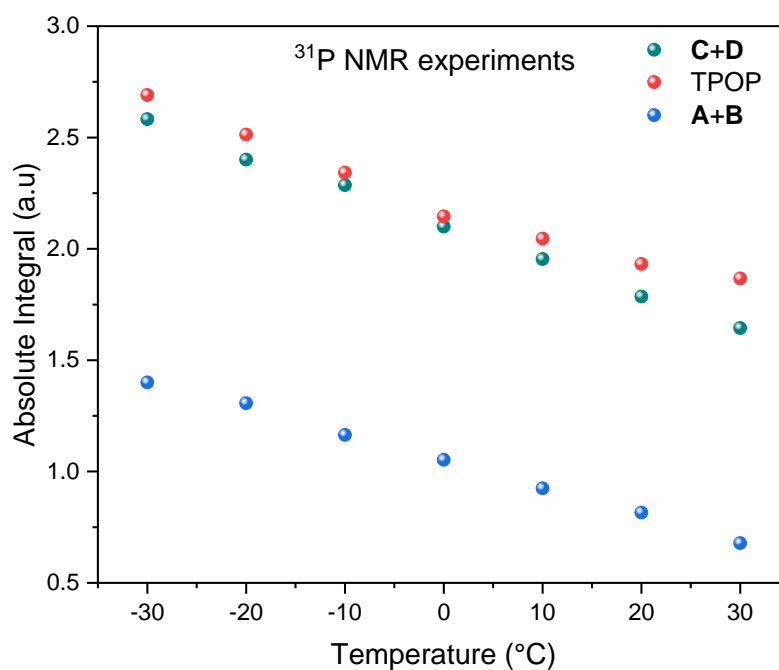
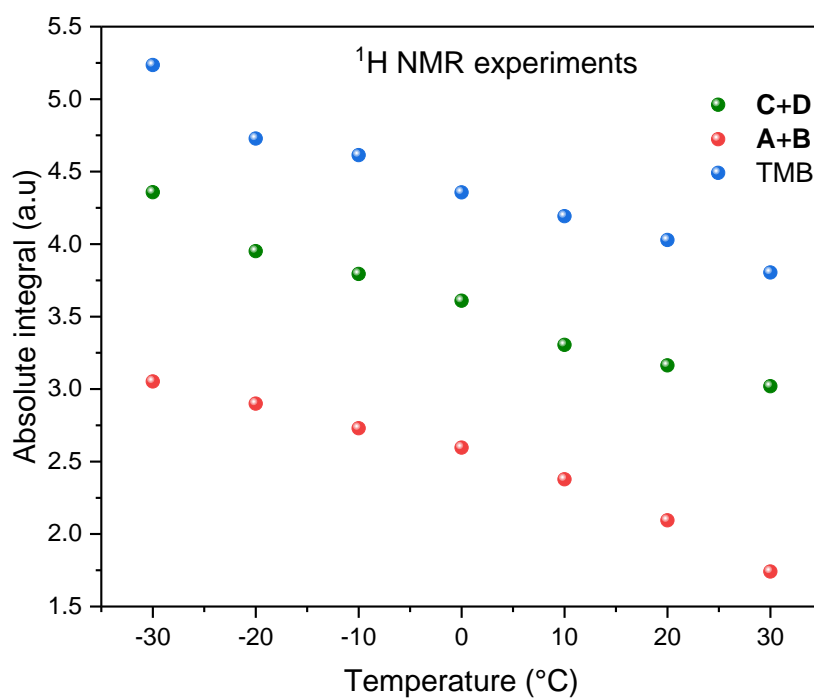


Figure S3. Absolute integral values of $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ (C/D), $[\text{RhH}(\text{CO})_2(\text{PPh}_3)_2]$ (A/B) and TMB obtained from selective excitation ^1H NMR spectroscopy (upper) and absolute integral of $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ (C/D), $[\text{RhH}(\text{CO})_2(\text{PPh}_3)_2]$ (A/B) and triphenylphosphate (TPOP) obtained from $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (lower) in the mixture containing 12.5 mM of $[\text{RhHCO}(\text{PPh}_3)_3]$, 10 mM of TMB and 10 mM of PPh_3 in 0.8 mL of non-deuterated toluene under 5 bar of CO and H_2 .

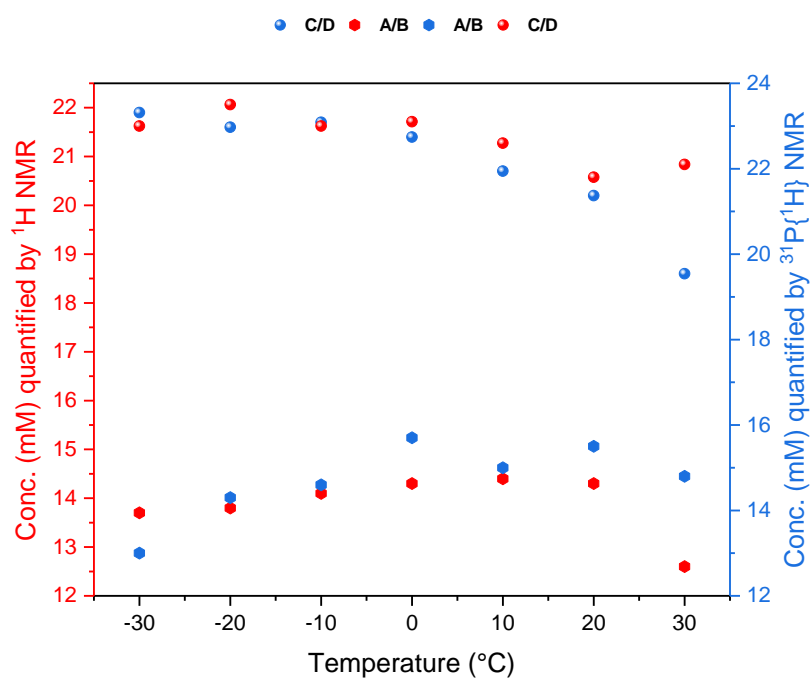


Figure S4. Concentration of $[\text{RhH}(\text{CO})(\text{PPh}_3)_3]$ (C/D) and $[\text{RhH}(\text{CO})_2(\text{PPh}_3)_2]$ (A/B) quantified by selective excitation ^1H NMR (upper) and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (lower) in the mixture containing 40 mM of $[\text{RhHCO}(\text{PPh}_3)_3]$, 10 mM of TMB and 10 mM of PPh_3 in 0.8 mL of non-deuterated toluene under 5 bar of CO and H_2 .

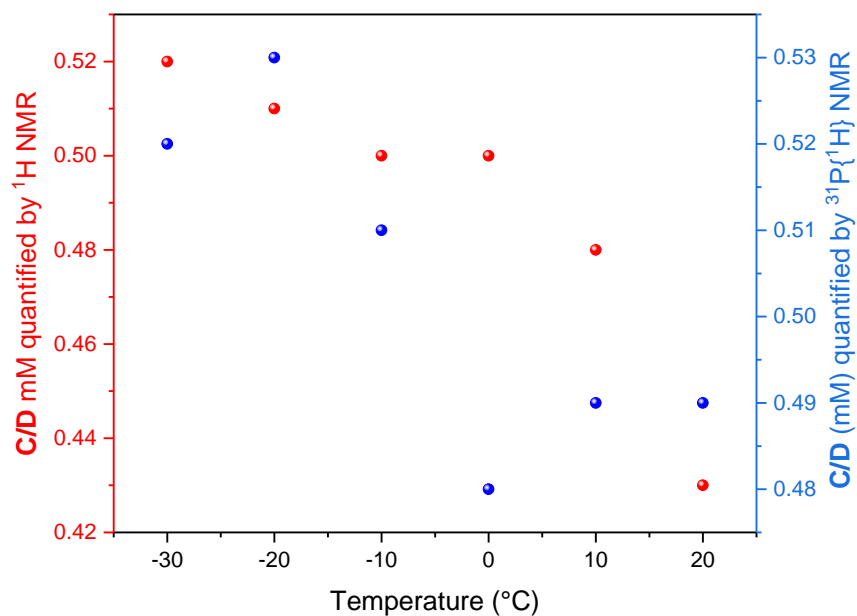


Figure S5. Concentration of C/D quantified by selective excitation ^1H NMR (upper) and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (lower) in the mixture containing 1 mM of $[\text{RhHCO}(\text{PPh}_3)_3]$, 1 mM of TMB and 10 mM of PPh_3 in 0.8 mL of non-deuterated toluene under argon.

$^{31}\text{P}\{^1\text{H}\}$ NMR

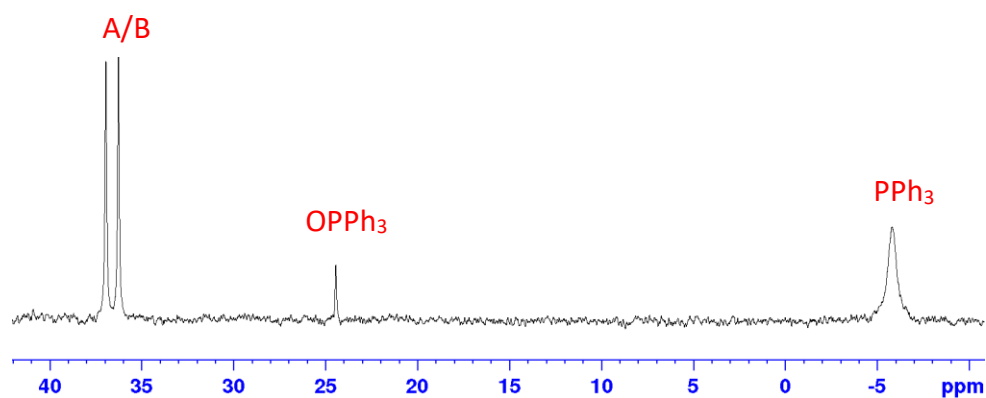


Figure S6. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded during the hydroformylation of 1-hexene under 12 bar of CO/H_2 (1:1) at 50°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 15\text{mM}$ (6 eq.) in 22.4 mL of non-deuterated toluene.

^1H NMR

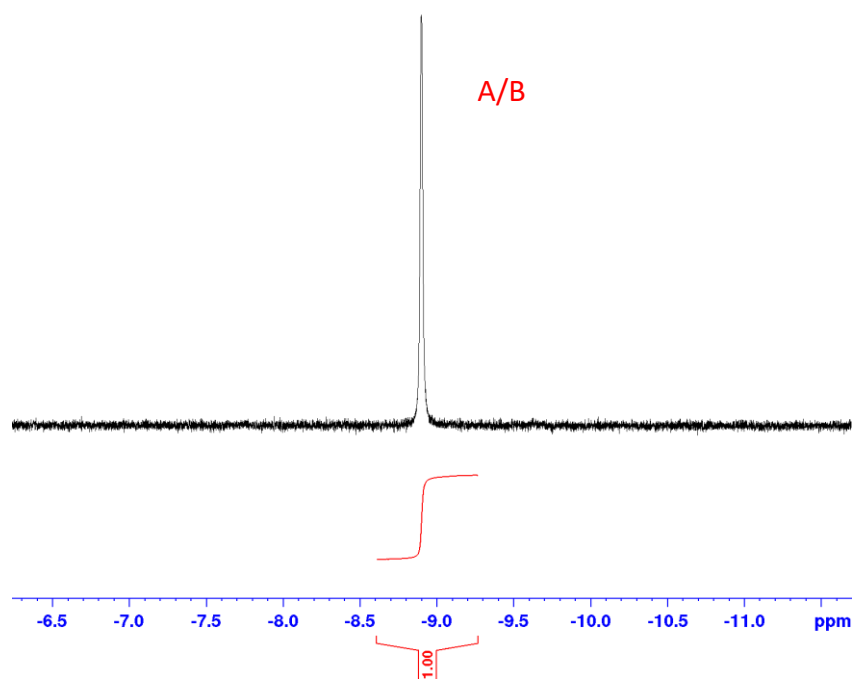


Figure S7. ^1H FlowNMR spectrum recorded during the hydroformylation of 1-hexene under 12 bar of CO/H_2 (1:1) at 50°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 15\text{mM}$ (6 eq.) in 22.4 mL of non-deuterated toluene.

$^{31}\text{P}\{^1\text{H}\}$ NMR

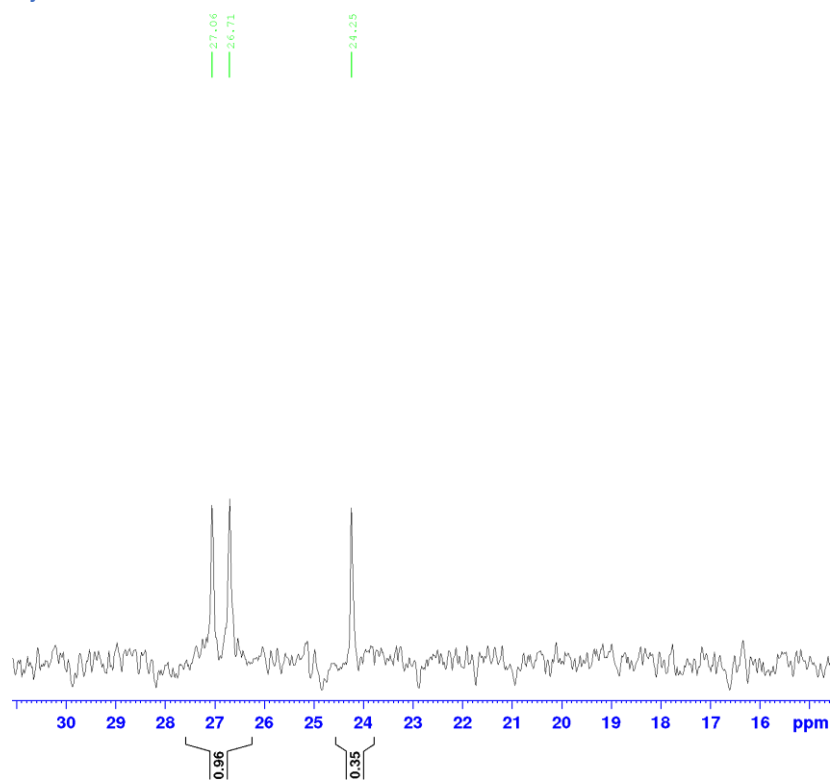


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded during the hydroformylation of 1-hexene under 12 bar of CO/H_2 (1:1) at 50°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 2.5\text{mM}$ (1 eq.) in 22.4 mL of non-deuterated toluene.

^1H NMR

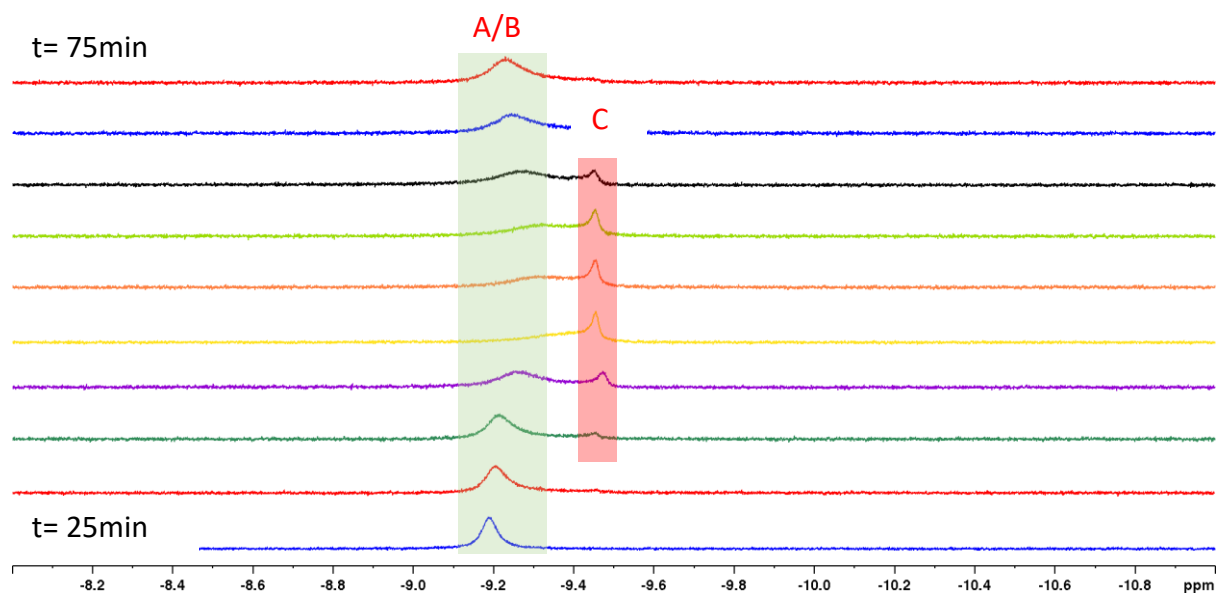


Figure S9. Selective excitation ^1H FlowNMR spectra recorded between 25 and 75 min during the hydroformylation of 1-hexene under 12 bar of CO/H_2 (1:3) at 50°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 15\text{mM}$ in 22.4 mL of non-deuterated toluene.

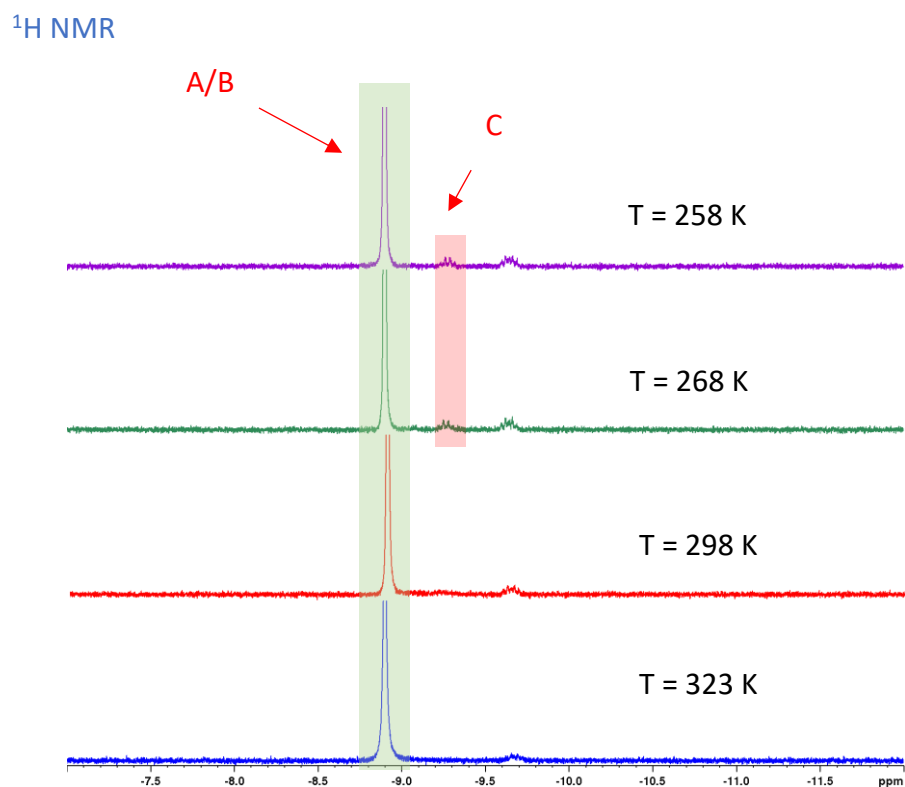
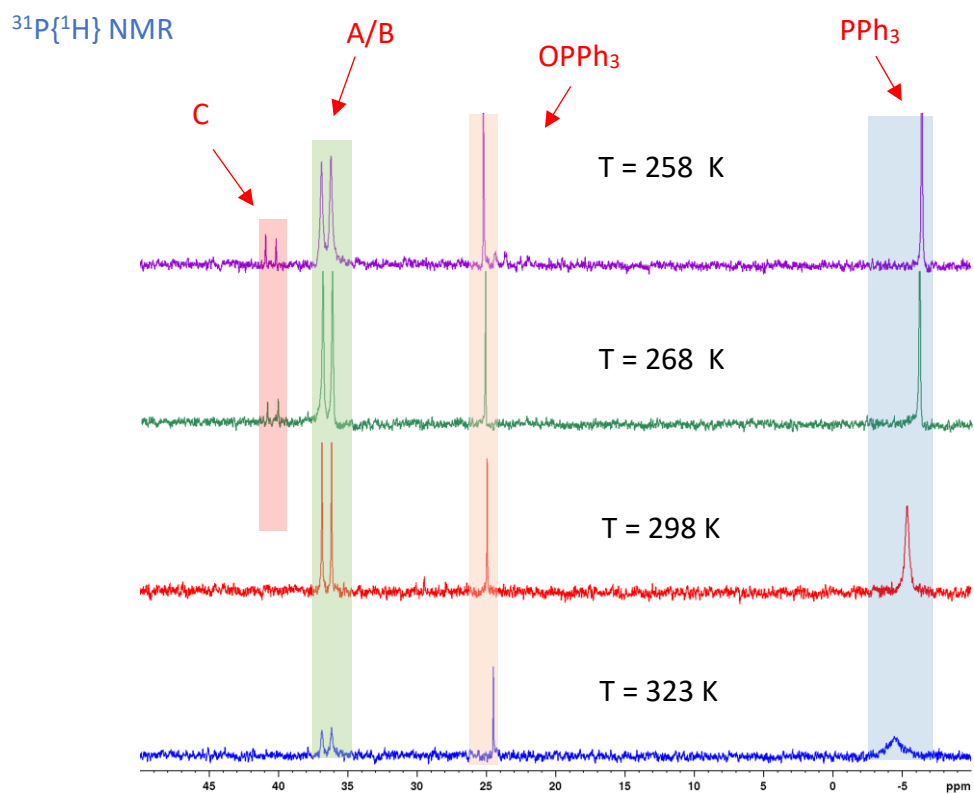


Figure S10. VT $^{31}\text{P}\{^1\text{H}\}$ (upper) and selective excitation ^1H NMR (lower) experiments on a reaction mixture from $[\text{Rh}(\text{CO})_2(\text{acac})] + 6 \text{PPh}_3$ catalysed hydroformylation of 1-hexene in 22.4 mL of non-deuterated toluene under 12 bar of H_2/CO (1:1) at $t = 330$ mins. $[\text{Rh}(\text{CO})_2(\text{acac})] = 2.5$ mM, $[1\text{-hexene}] = 500$ mM, $[\text{PPh}_3] = 15$ mM and $[\text{TMB}] = 100$ mM.

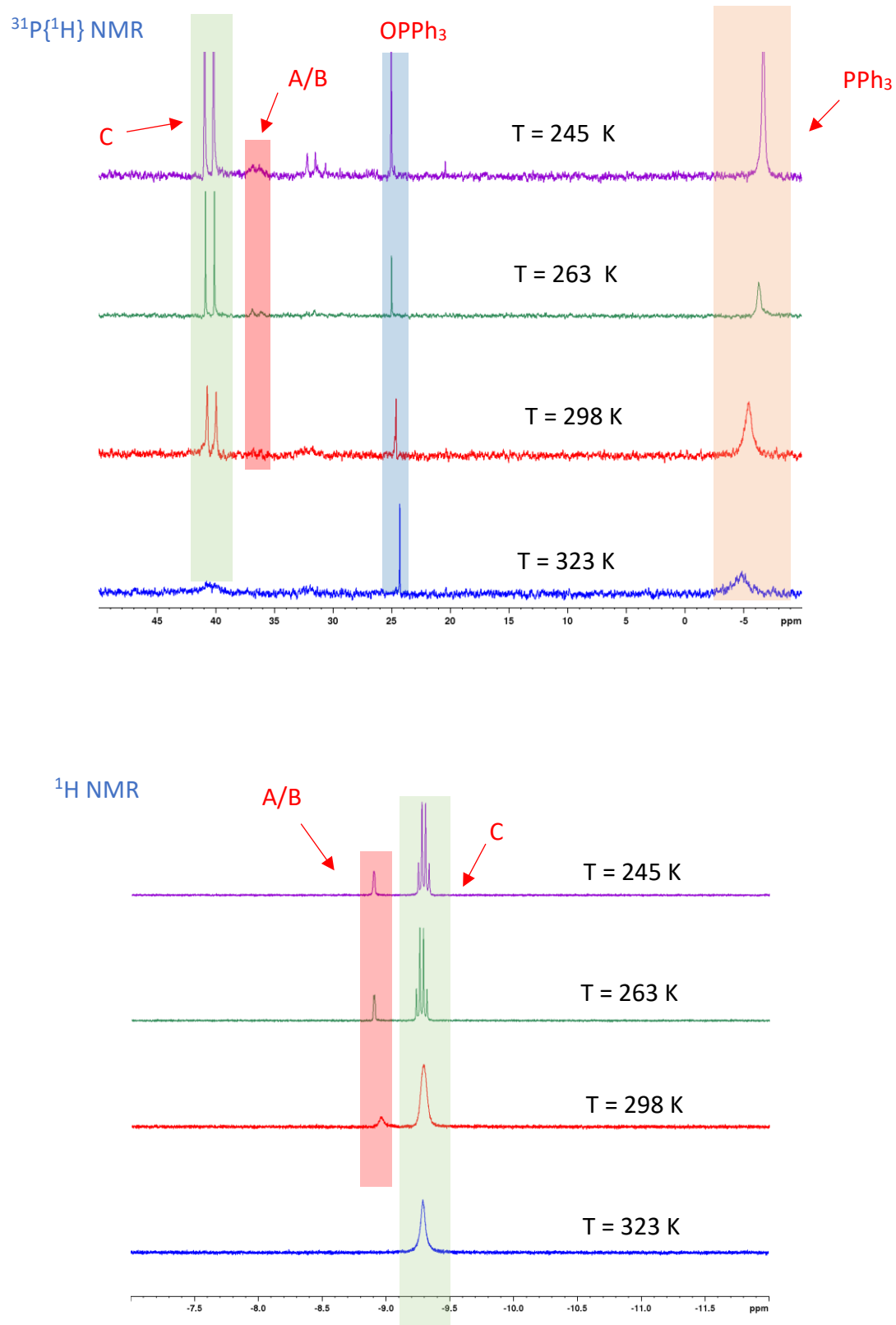


Figure S11. VT $^{31}\text{P}\{^1\text{H}\}$ and selective excitation ^1H NMR experiments of hydroformylation of 1-hexene under 12 bar of H_2/CO (1:1) using $[\text{Rh}] = 2.5 \text{ mM}$, $[\text{1-hexene}] = 500 \text{ mM}$, $[\text{TMB}] = 100 \text{ mM}$ and $[\text{PPh}_3] = 15 \text{ mM}$. The experiments were recorded under Ar after the reaction was finished and vented.

$^{31}\text{P}\{^1\text{H}\}$ NMR

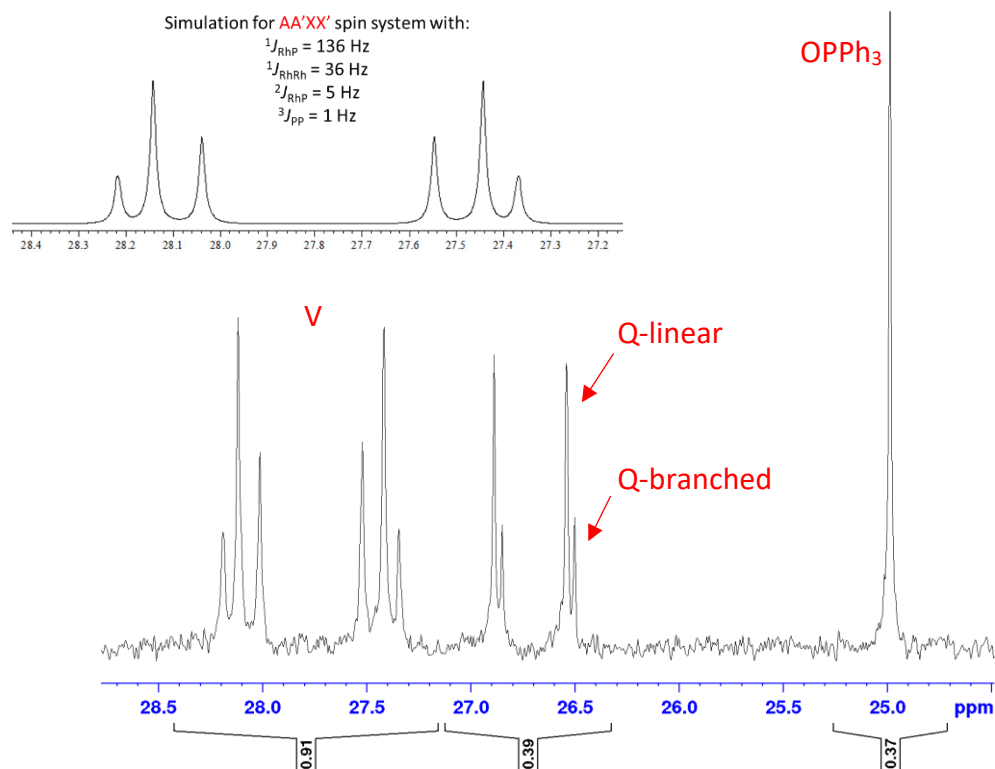


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:1) at 0°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5 \text{ mM}$ and $\text{PPh}_3 = 2.5 \text{ mM}$ (1 eq.) in 22.4 mL of non-deuterated toluene.

$^{31}\text{P}\{^1\text{H}\}$ NMR

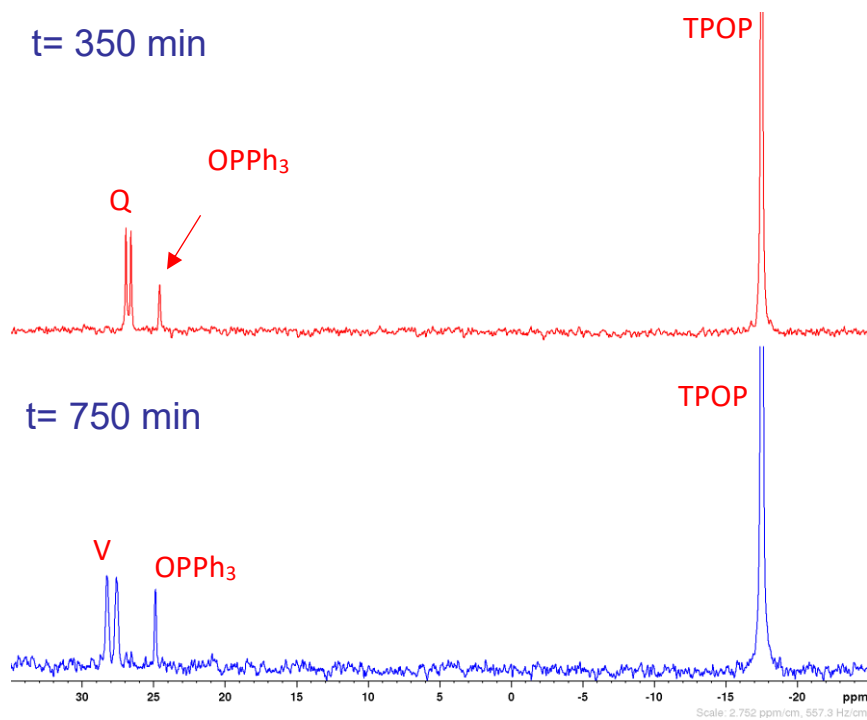


Figure S13. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectra recorded at different times during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:1) at 0°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5 \text{ mM}$ and $\text{PPh}_3 = 2.5 \text{ mM}$ (1 eq.) in 22.4 mL of non-deuterated toluene.

$^{31}\text{P}\{^1\text{H}\}$ NMR

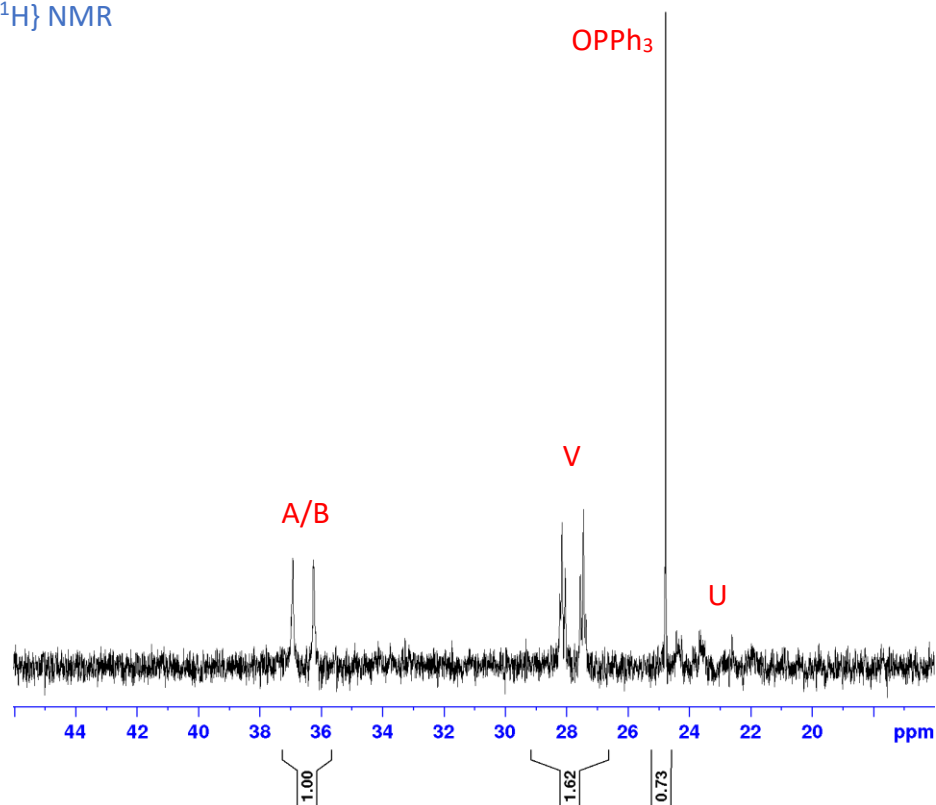


Figure S14. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:1) at 0°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 5.0\text{ mM}$ (2 eq.) in 22.4 mL of non-deuterated toluene.

$^{31}\text{P}\{^1\text{H}\}$ NMR

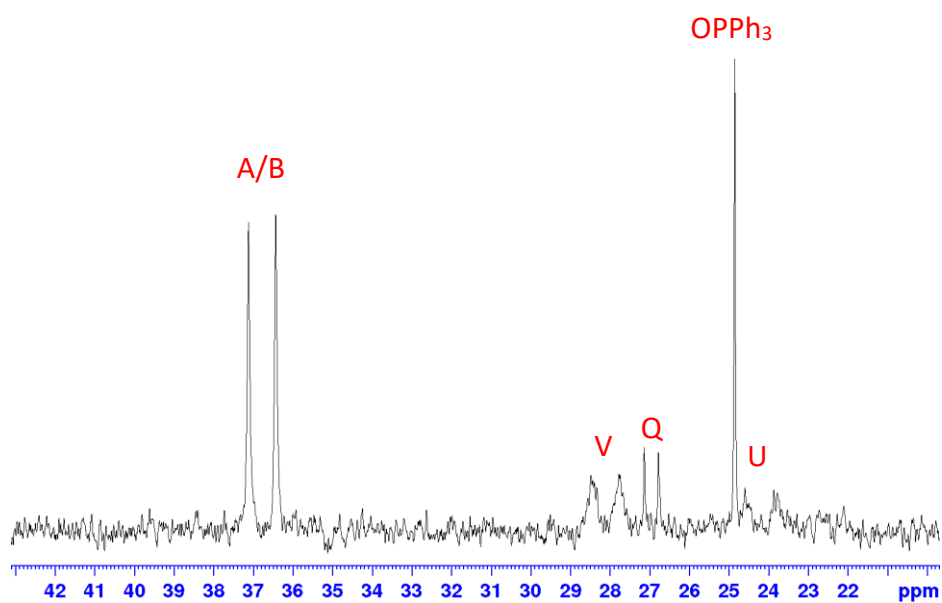


Figure S15. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:1) at 0°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 7.5\text{ mM}$ (3 eq.) in 22.4 mL of non-deuterated toluene.

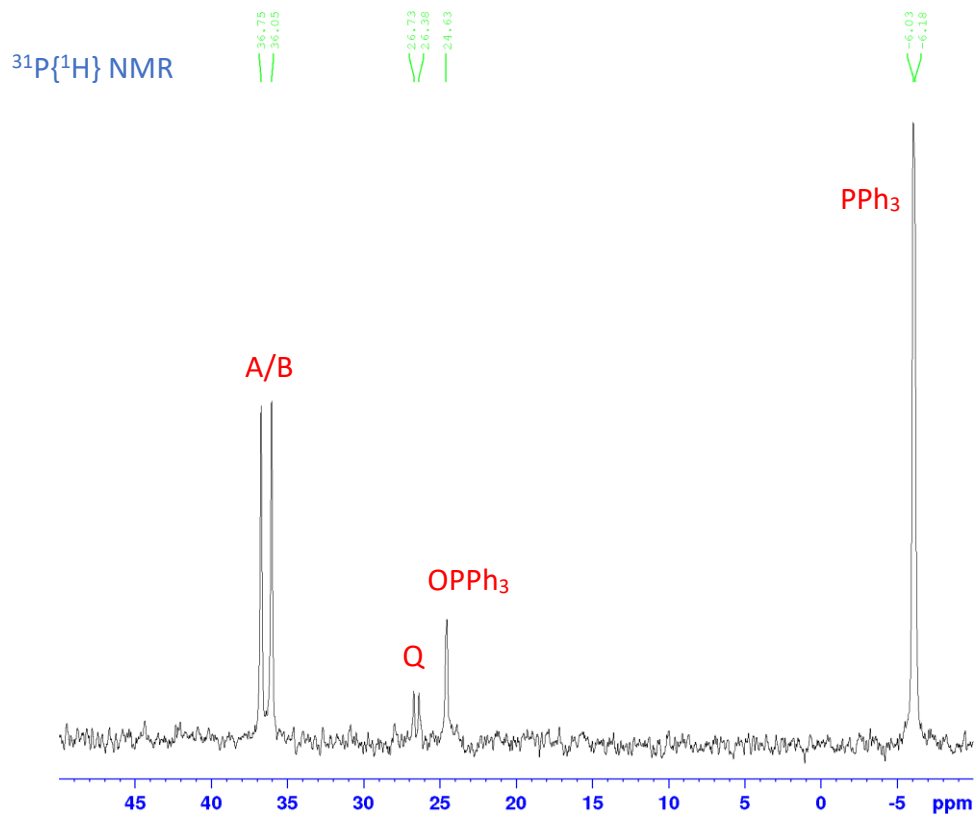


Figure S16. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:1) at 0°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 15\text{mM}$ (6 eq.) in 22.4 mL of non-deuterated toluene.

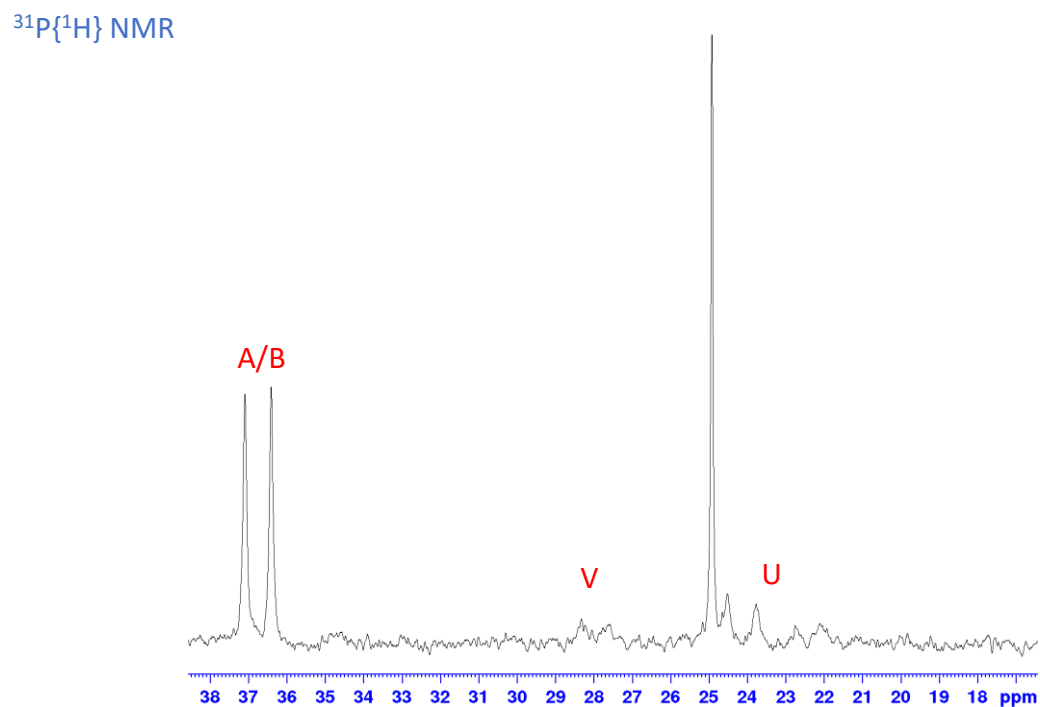


Figure S17. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:1) at 0°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 15\text{mM}$ (6 eq.) in 22.4 mL of non-deuterated toluene.

$^{31}\text{P}\{^1\text{H}\}$ NMR

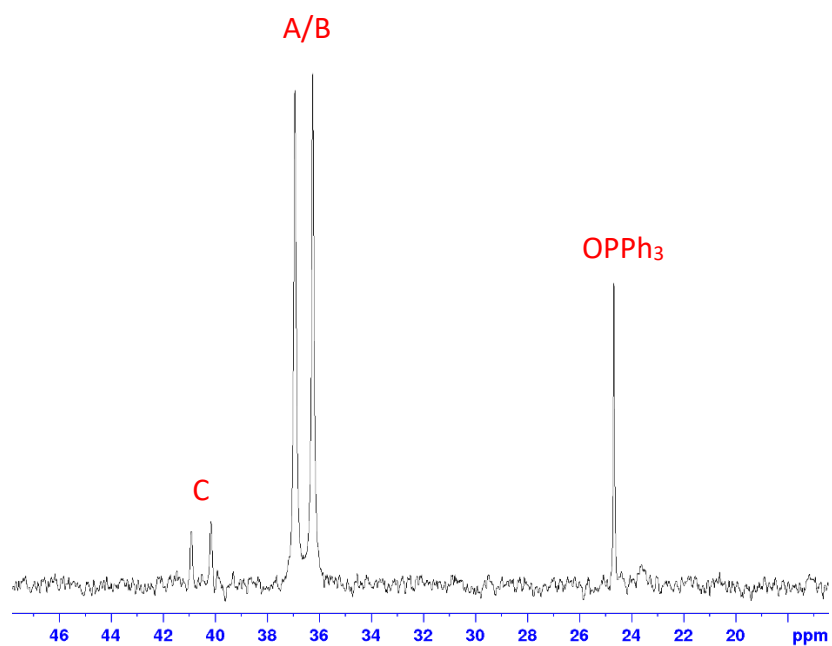


Figure S18. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum recorded during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:3) at 0°C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5\text{mM}$ and $\text{PPh}_3 = 15\text{mM}$ (6 eq.) in 22.4 mL of non-deuterated toluene.

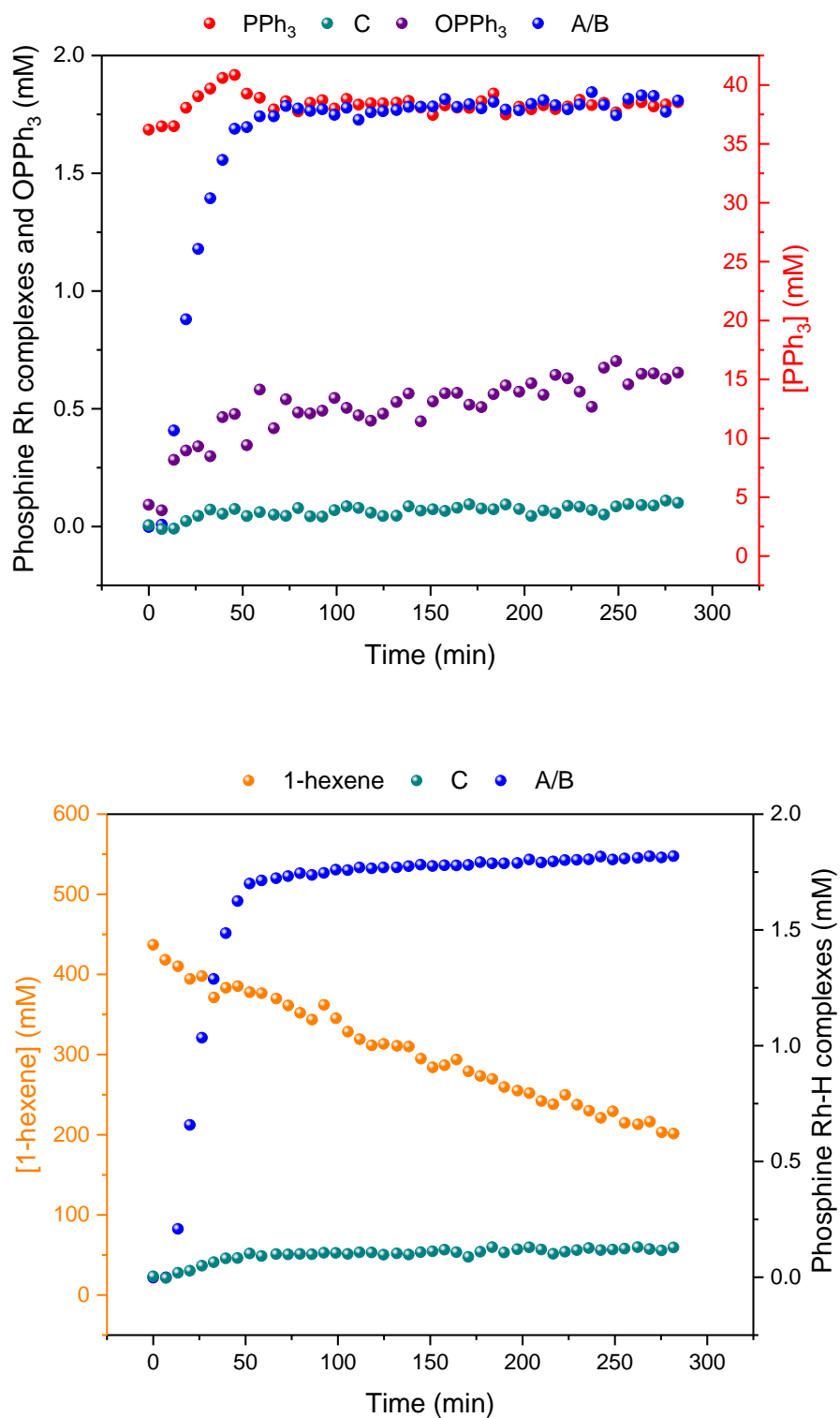


Figure S19. Profiles of catalyst species from quantitative $^{31}\text{P}\{^1\text{H}\}$ FlowNMR (upper) and 1-hexene concentration from quantitative ^1H FlowNMR (lower) during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:3) at 50 °C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5$ mM and $[\text{PPh}_3] = 50$ mM in 22.4 mL of non-deuterated toluene using the temperature gradients shown in Figure 7.

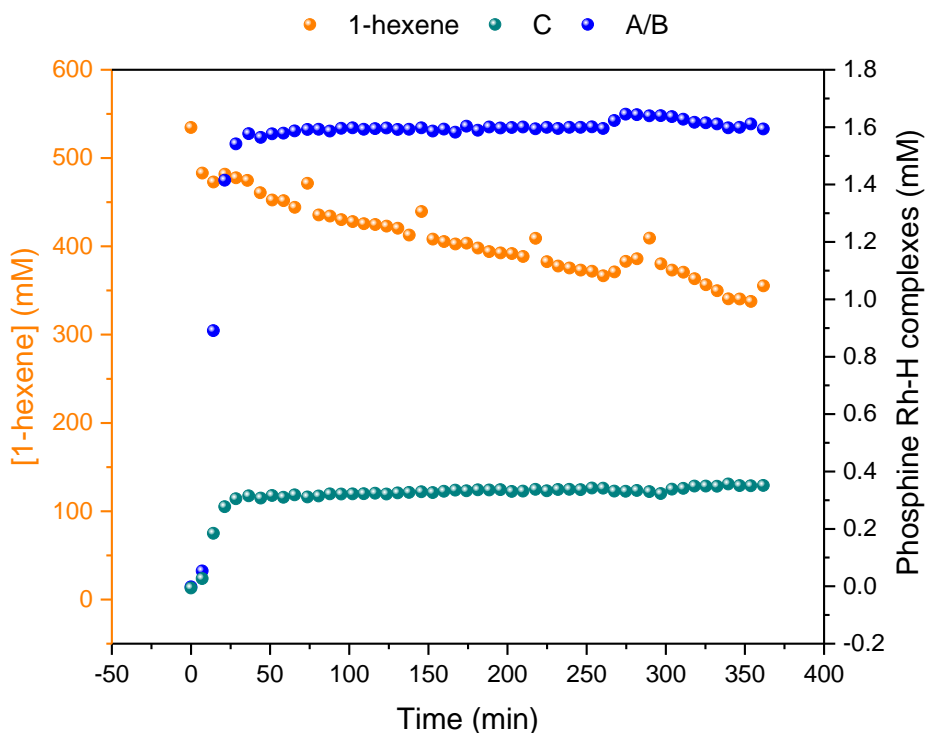
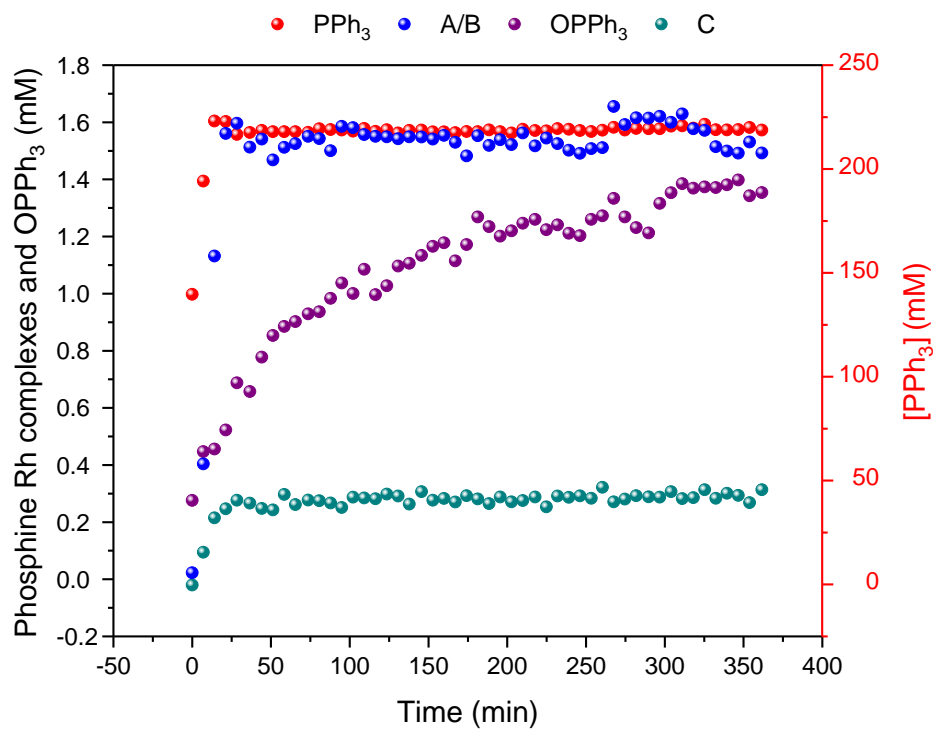


Figure S20. Profiles of catalyst species from quantitative $^{31}\text{P}\{^1\text{H}\}$ FlowNMR (upper) and 1-hexene concentration from quantitative ^1H FlowNMR (lower) during the hydroformylation of 1-hexene under 10 bar of CO/H_2 (1:3) at 50 °C catalysed by $[\text{Rh}(\text{acac})(\text{CO})_2] = 2.5 \text{ mM}$ and $[\text{PPh}_3] = 250 \text{ mM}$ in 22.4 mL of non-deuterated toluene using the temperature gradients shown in Figure 7.

$^{31}\text{P}\{^1\text{H}\}$ NMR

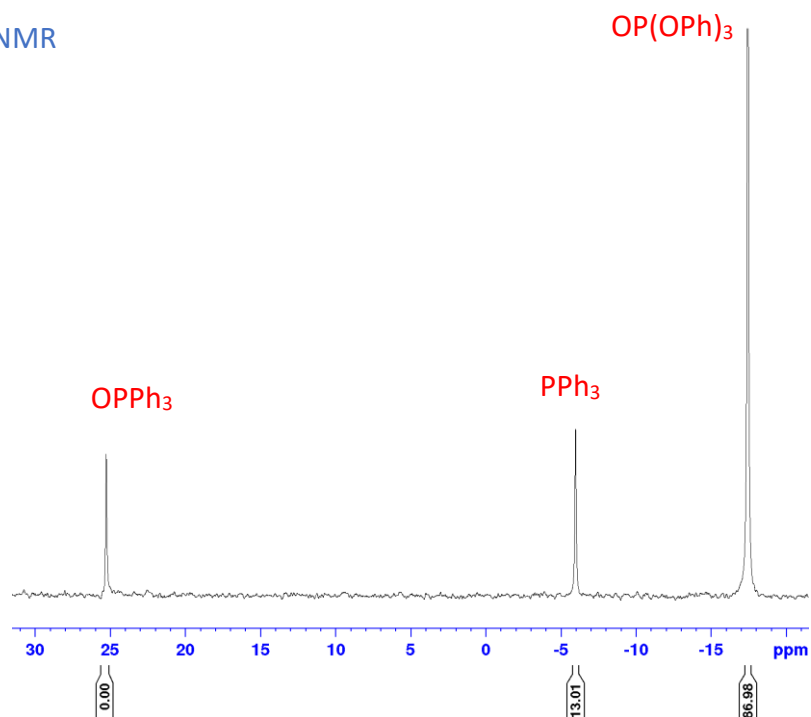


Figure S21. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded at $-30\text{ }^\circ\text{C}$ for the reaction of $\text{Rh}(\text{acac})_3$ (2.5 mM) with three equivalents of PPh_3 (7.5 mM) in 22.4 mL of non-deuterated toluene under 10 bar of CO and H_2 . The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

$^{31}\text{P}\{^1\text{H}\}$ NMR

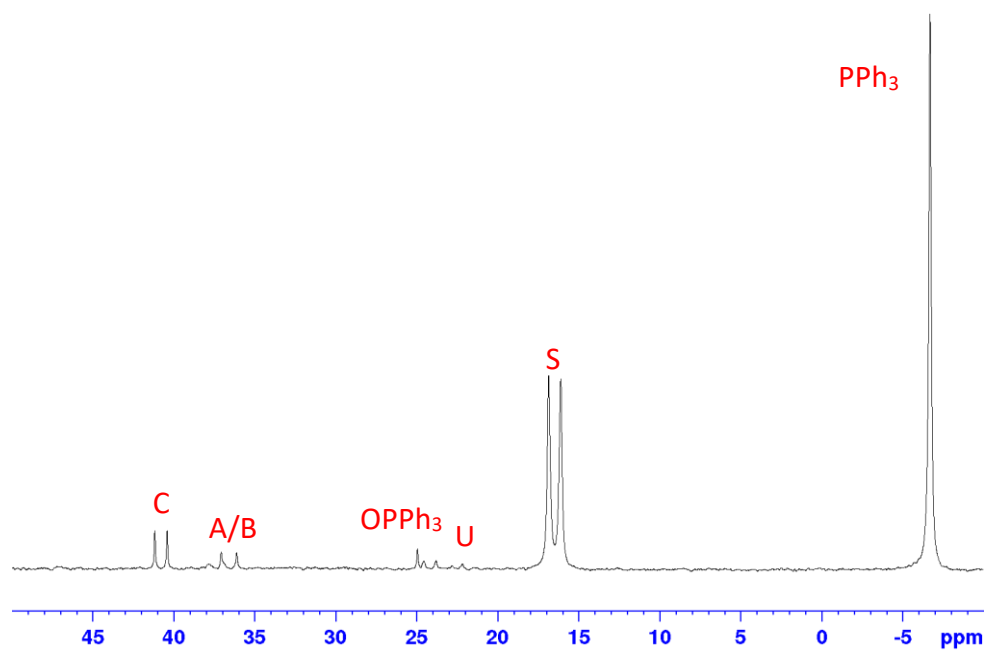


Figure S22. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded at $-10\text{ }^\circ\text{C}$ from the reaction of $[\text{Rh}_4\text{CO}_{12}]$ (2.5 mM) with 12 equivalents of PPh_3 (30 mM) in 22.4 mL of non-deuterated toluene under argon. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

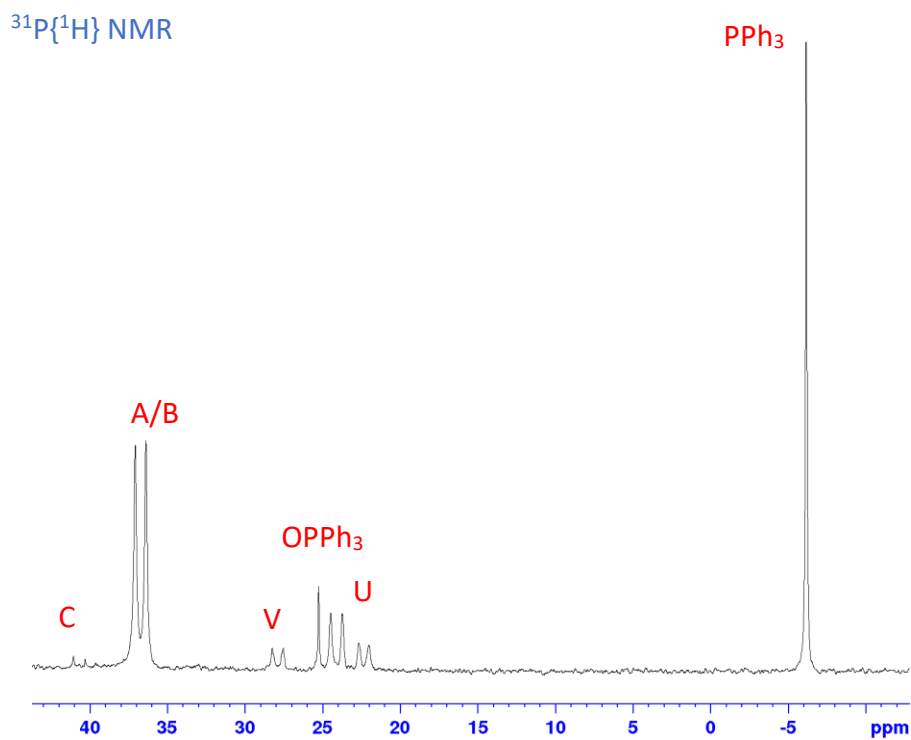


Figure S23. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded at -10°C from the reaction of $[\text{Rh}_4\text{CO}_{12}]$ (2.5 mM) with 12 equivalents of PPh_3 (30 mM) in 22.4 mL of non-deuterated toluene under 10 bar of CO and H_2 . The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

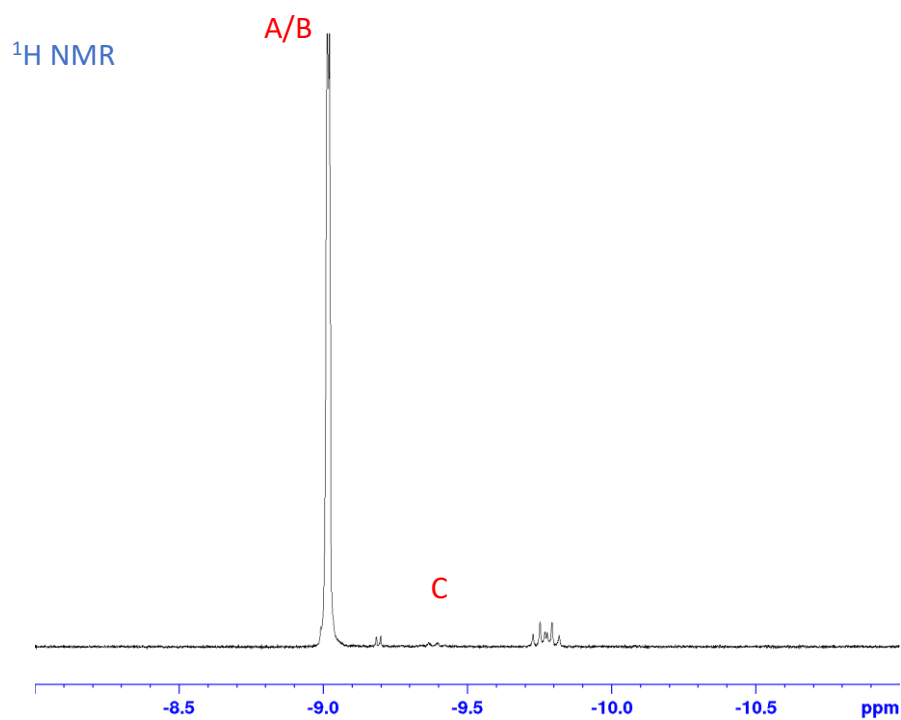


Figure S24. ^1H FlowNMR spectrum recorded at -10°C from the reaction of $[\text{Rh}_4\text{CO}_{12}]$ (2.5 mM) with 12 equivalents of PPh_3 (30 mM) in 22.4 mL of non-deuterated toluene under 10 bar of CO and H_2 . The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

$^{31}\text{P}\{^1\text{H}\}$ NMR

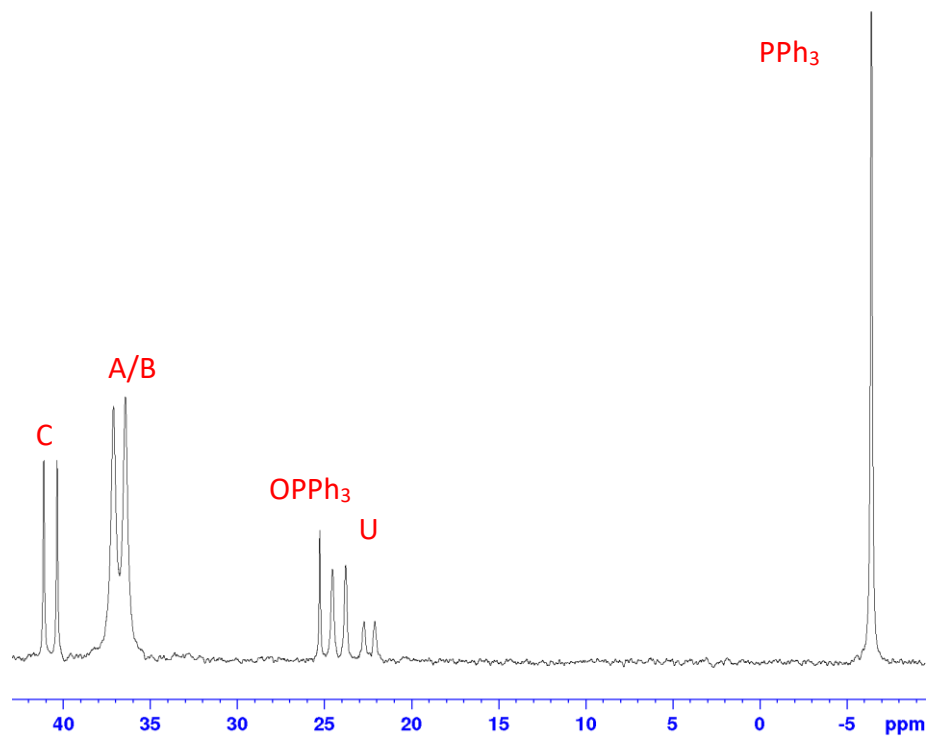


Figure S25. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded at -10°C from the reaction of $[\text{Rh}_4\text{CO}_{12}]$ (2.5 mM) with 12 equivalents of PPh_3 (30 mM) in 22.4 mL of non-deuterated toluene under Ar after having vented the reactor that contained syngas. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

^1H NMR

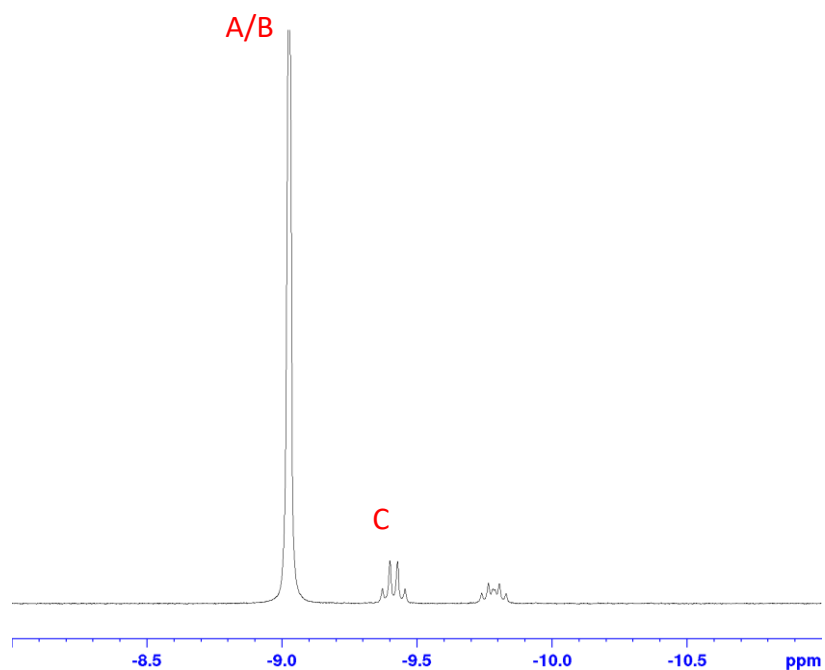


Figure S26. ^1H FlowNMR spectrum recorded at -10°C from the reaction of $[\text{Rh}_4\text{CO}_{12}]$ (2.5 mM) with 12 equivalents of PPh_3 (30 mM) in 22.4 mL of non-deuterated toluene under Ar after having vented the reactor that contained syngas. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

$^{31}\text{P}\{^1\text{H}\}$ NMR

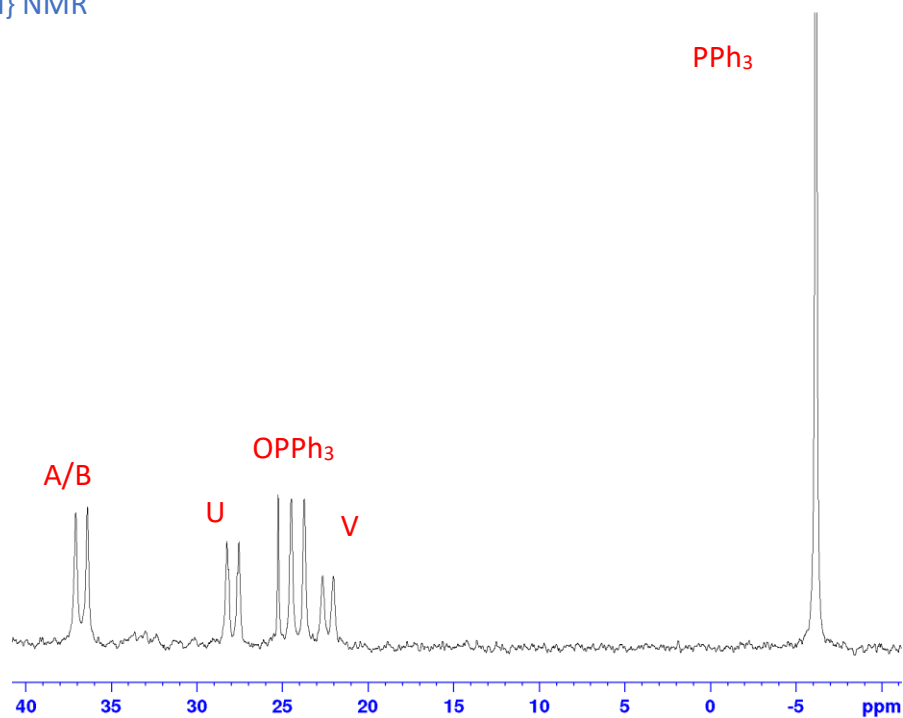


Figure S27. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded at -10°C from the reaction of $[\text{Rh}_4\text{CO}_{12}]$ (2.5 mM) with 12 equivalents of PPh_3 (30 mM) in 22.4 mL of non-deuterated toluene under 10 bar of CO. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

$^{31}\text{P}\{^1\text{H}\}$ NMR

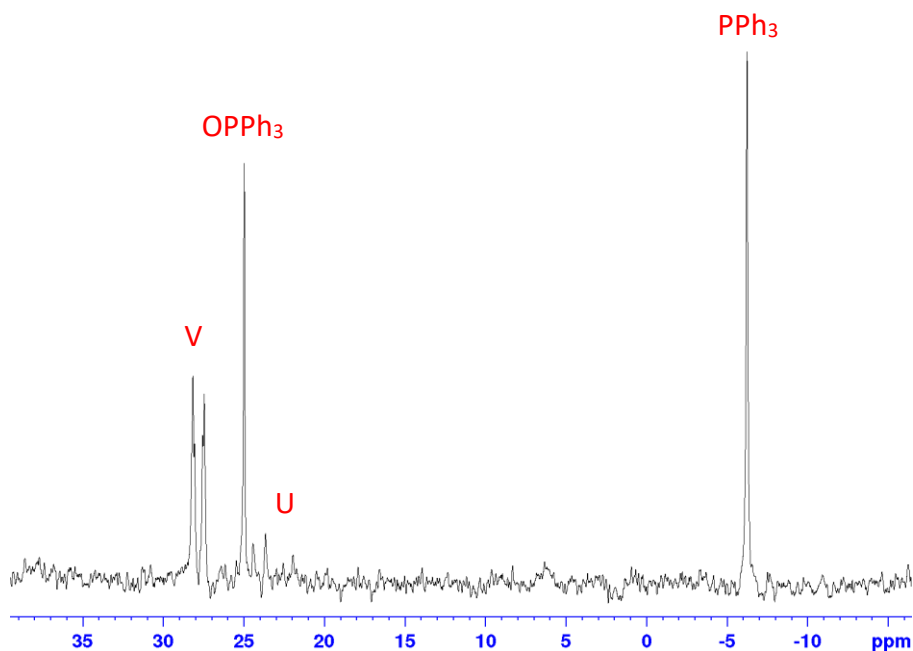


Figure S 28. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded of the reaction of **C** (2.5 mM) without added equivalents of PPh_3 in 22.4 mL of non-deuterated toluene under 10 bar of CO at -10°C . The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

$^{31}\text{P}\{^1\text{H}\}$ NMR

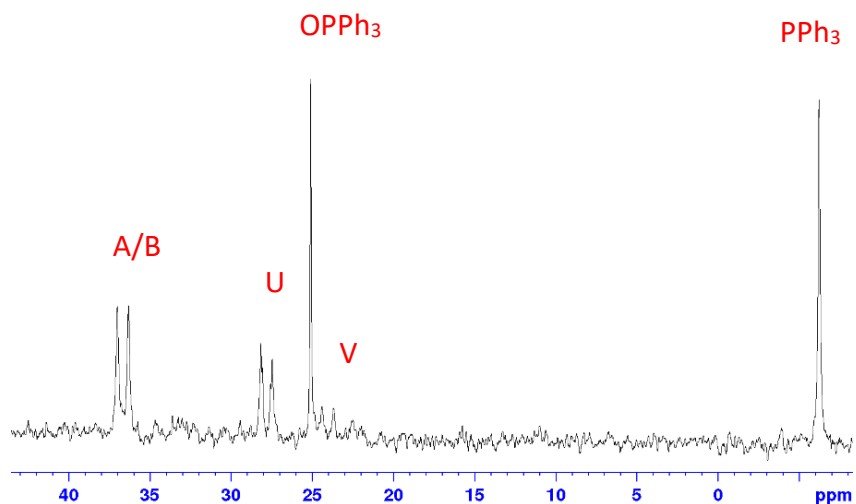


Figure S29. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded of the reaction of **C** (2.5 mM) without added equivalents of PPh_3 in 22.4 mL of non-deuterated toluene under 10 bar of CO and H_2 at -10°C . The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

^1H NMR

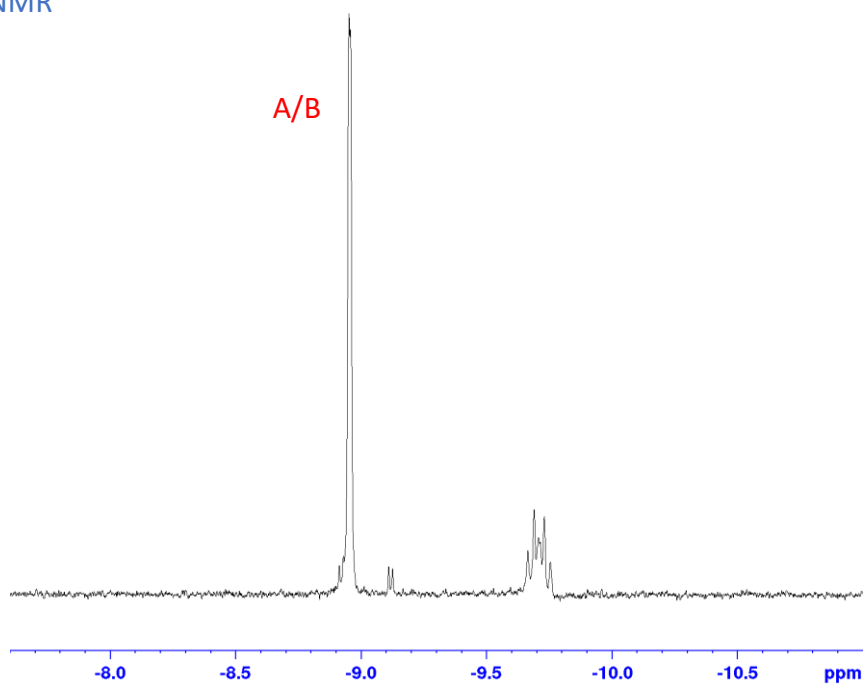


Figure S30. ^1H FlowNMR spectrum recorded of the reaction of **C** (2.5 mM) without added equivalents of PPh_3 in 22.4 mL of non-deuterated toluene under 10 bar of CO and H_2 at -10°C . The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

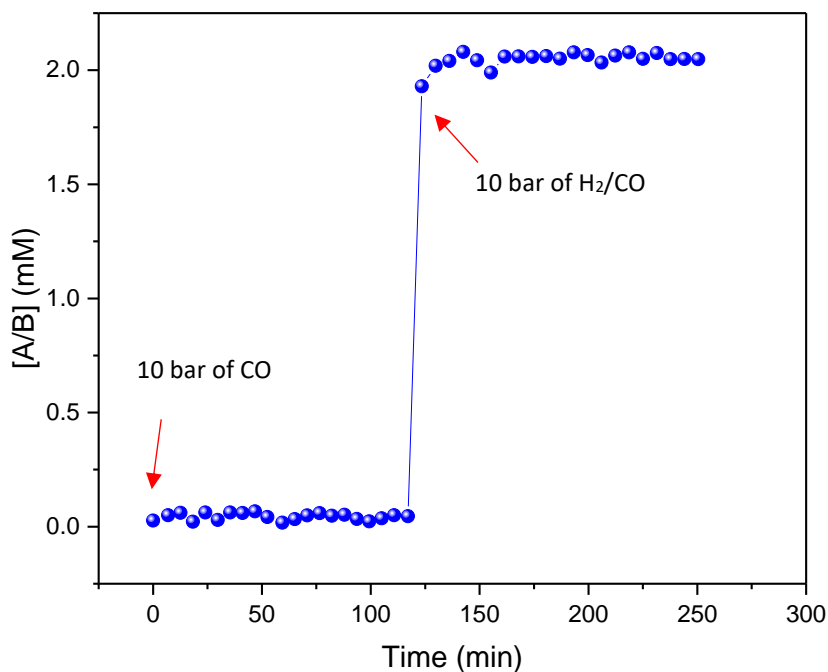


Figure S31. Amount A/B followed by ^1H FlowNMR during the reaction of **C** (2.5 mM) without added PPh_3 in 22.4 mL of non-deuterated toluene under 10 bar of CO/H_2 (1:1) at 50°C .

$^{31}\text{P}\{^1\text{H}\}$ NMR

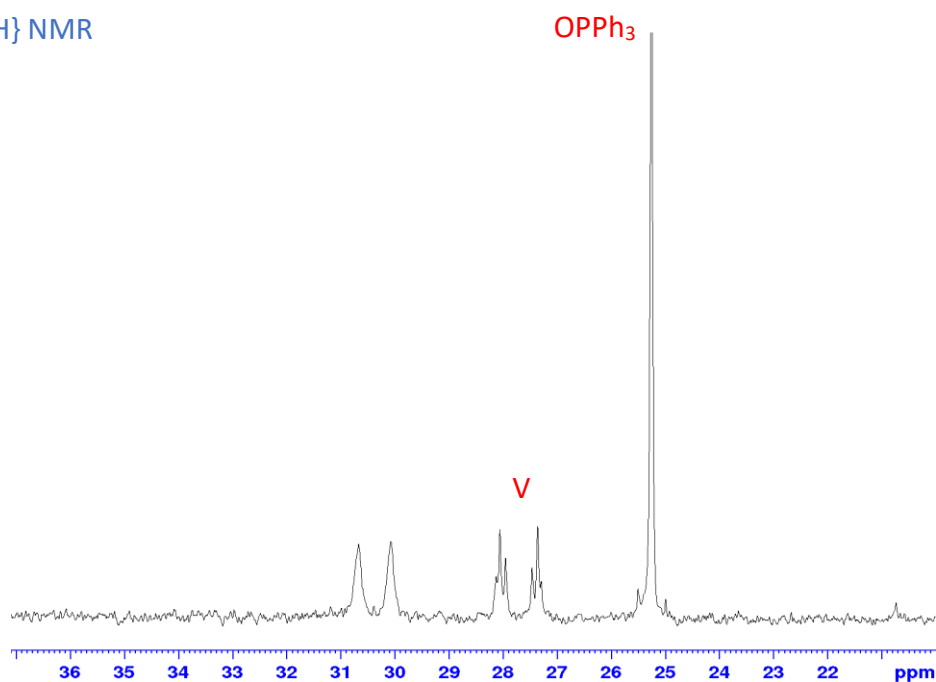


Figure S32. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded of the reaction of **3** (2.5 mM) with three equivalents of PPh_3 (7.5 mM) in 22.4 mL of non-deuterated toluene under 10 bar of CO and H_2 (1:1) at -30°C after 700 min of pressurising the reactor. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

$^{31}\text{P}\{^1\text{H}\}$ NMR

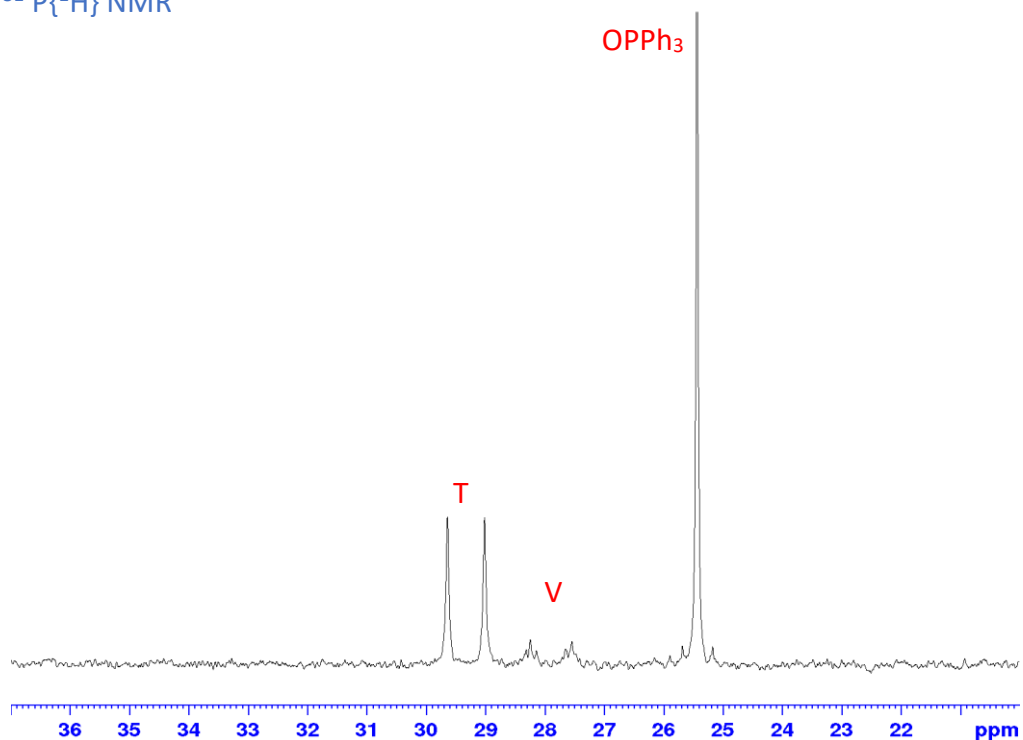


Figure S33. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded at $-30\text{ }^\circ\text{C}$ of the reaction of **3** (2.5 mM) with three equivalents of PPh_3 (7.5 mM) in 22.4 mL of non-deuterated toluene under 10 bar of H_2 after having purged the autoclave. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

$^{31}\text{P}\{^1\text{H}\}$ NMR

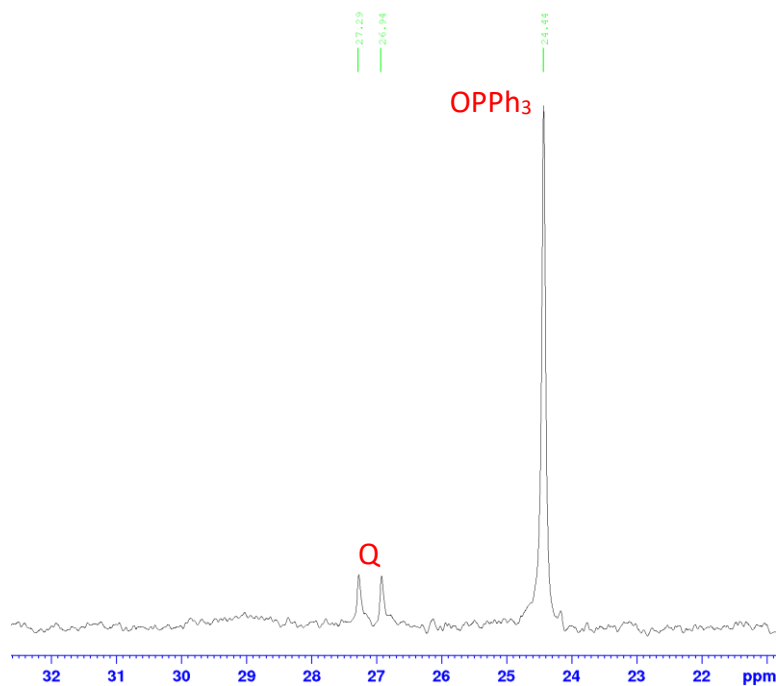


Figure S34. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded at $-30\text{ }^\circ\text{C}$ of the reaction of **3** (2.5 mM) with three equivalents of PPh_3 (7.5 mM) in 22.4 mL of non-deuterated toluene under 10 bar of CO and H_2 after having added 1-hexene. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

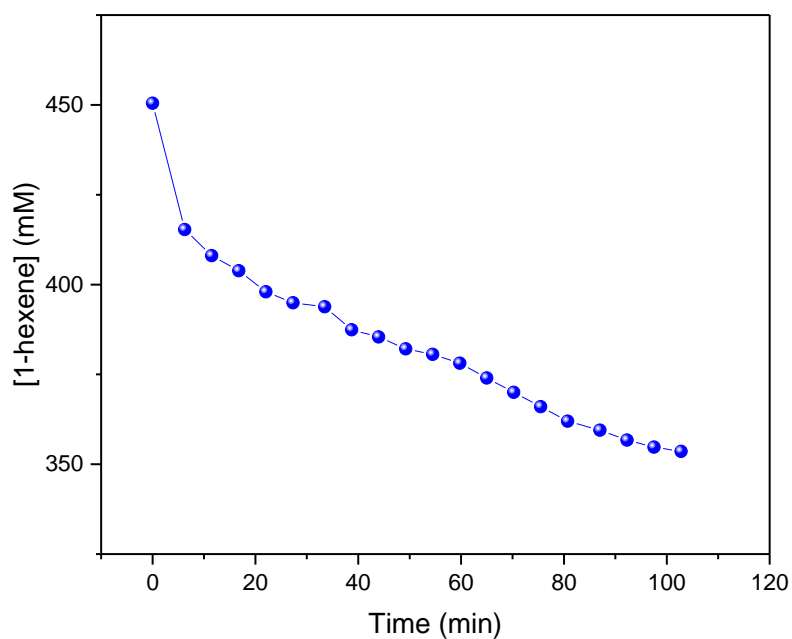


Figure S35. Consumption of 1-hexene recorded by ^1H FlowNMR at 50°C during the reaction of $\text{Rh}(\text{acac})(\text{CO})_2$ (2.5 mM) with three equivalents of PPh_3 (7.5 mM) in 22.4 mL of non-deuterated toluene under 10 bar of CO and H_2 after having added 1-hexene.

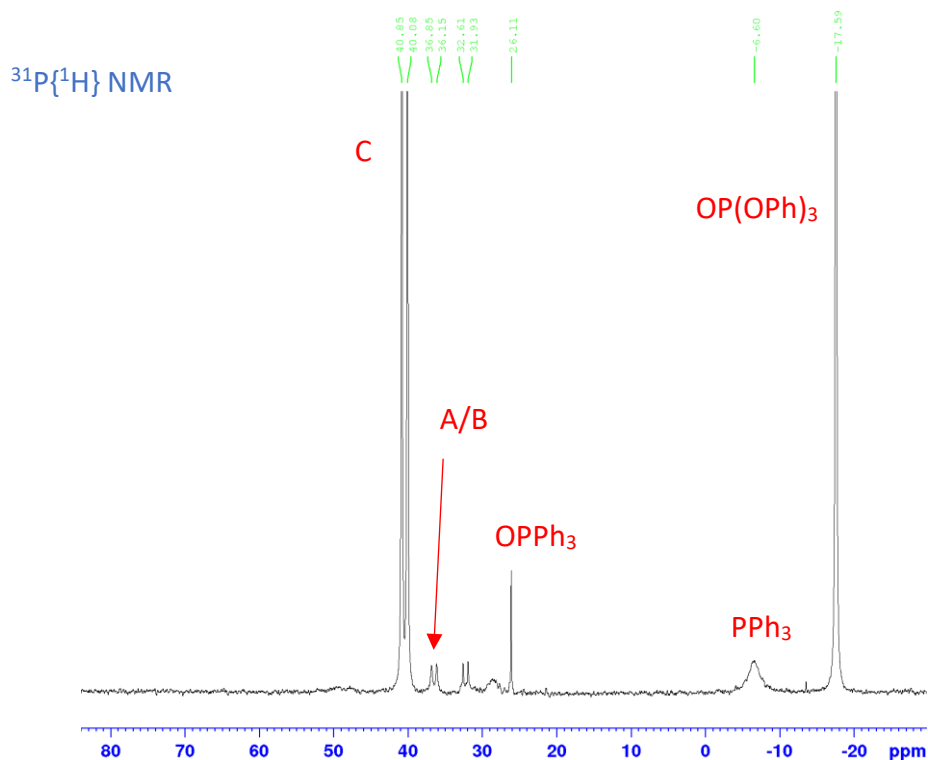


Figure S36. $^{31}\text{P}\{^1\text{H}\}$ FlowNMR spectrum recorded of the reaction of $[\text{Rh}(\text{acac})(\text{CO})_2]$ (2.5 mM) with three equivalents of PPh_3 (7.5 mM) in 22.4 mL of non-deuterated toluene under 10 bar of H_2 at -30°C after 1000 min of pressurising the reactor. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

^1H NMR

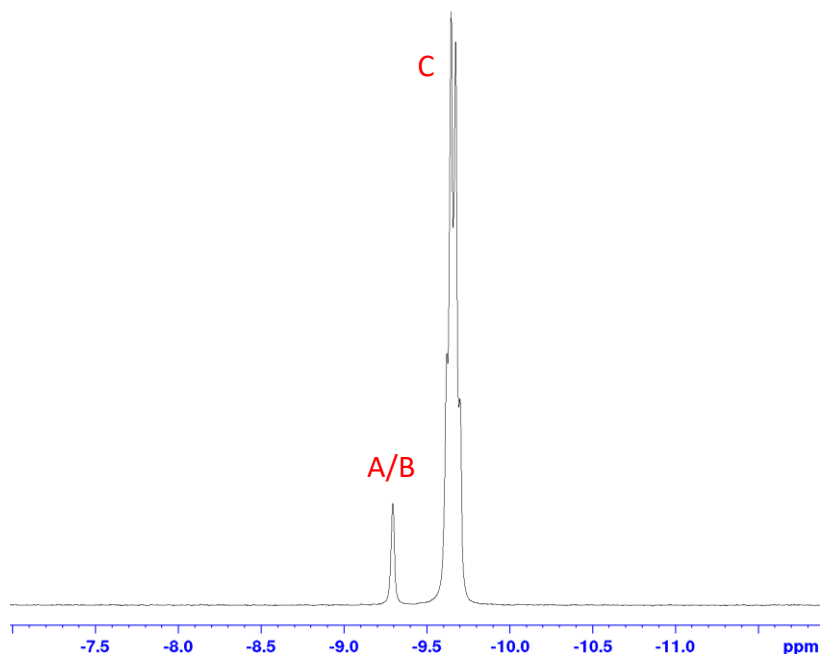


Figure S37. Selective excitation ^1H FlowNMR spectrum recorded of the reaction of $[\text{Rh}(\text{acac})(\text{CO})_2]$ (2.5 mM) with three equivalents of PPh_3 (7.5 mM) in 22.4 mL of non-deuterated toluene under 10 bar of H_2 at $-30\text{ }^\circ\text{C}$ after 1000 min of pressurising the reactor. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

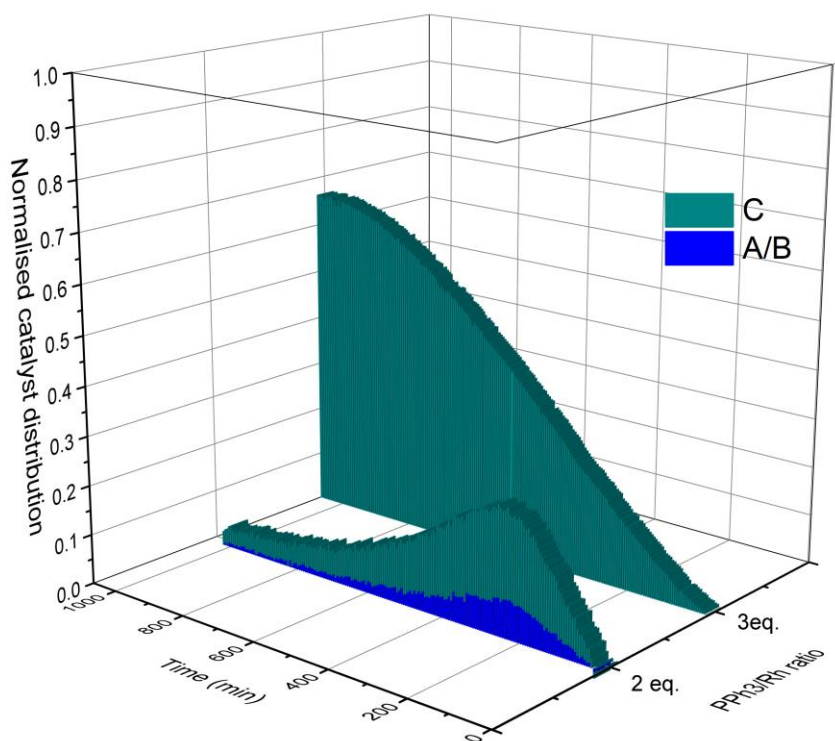


Figure S38. Activation of **3** at 2.5 mM in toluene with 2 and 3 equivalents of PPh_3 under 10 bar H_2 at $50\text{ }^\circ\text{C}$ as derived from quantitative FlowNMR spectroscopy.

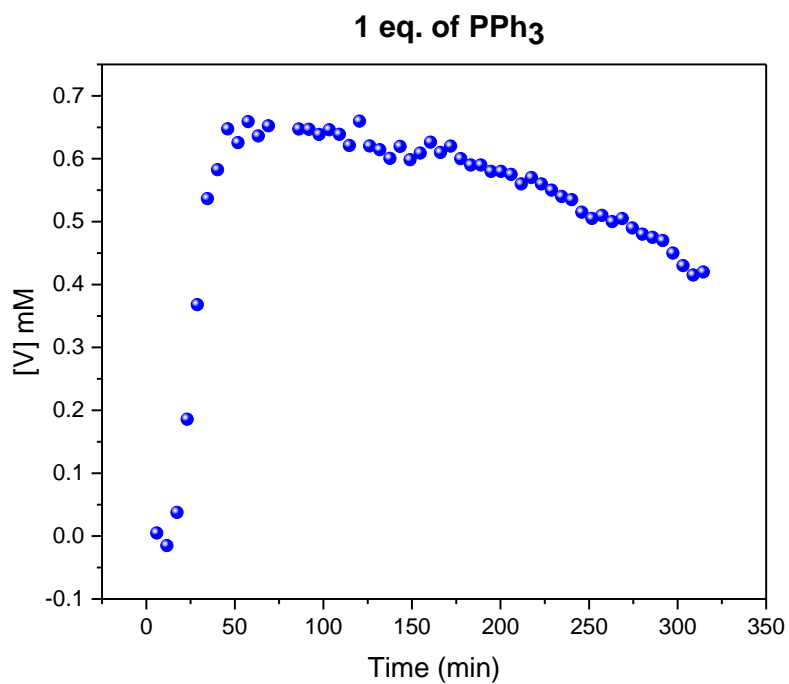


Figure S39. Concentration profiles for the reaction of **[2]** = 2.5 mM with 2 equivalents of PPh₃ in 22.4 mL of non-deuterated toluene under 10 bar of CO and H₂ at 50 °C as derived from quantitative FlowNMR spectroscopy.

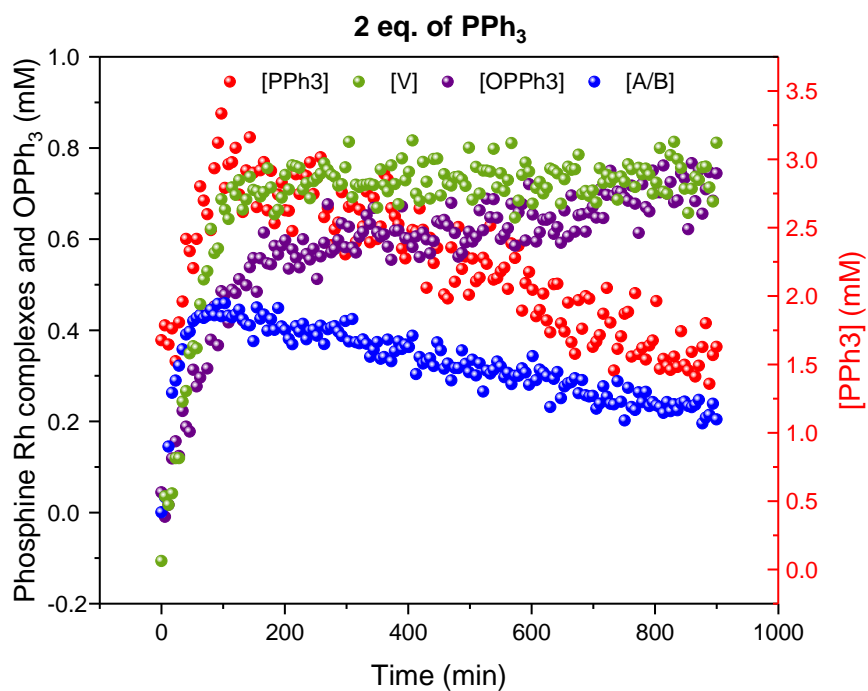


Figure S40. Concentration profiles for the reaction of **[2]** = 2.5 mM with 2 equivalents of PPh₃ in 22.4 mL of non-deuterated toluene under 10 bar of CO and H₂ at 50 °C as derived from quantitative FlowNMR spectroscopy.

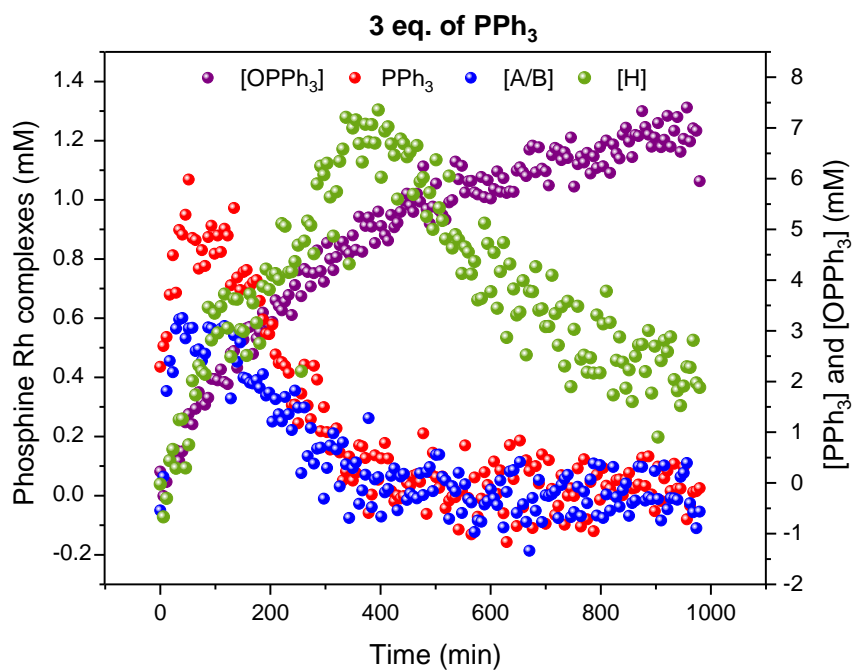


Figure S41. Concentration profiles for the reaction of **[2]** = 2.5 mM with 3 equivalents of PPh₃ in 22.4 mL of non-deuterated toluene under 10 bar of CO and H₂ at 50 °C as derived from quantitative FlowNMR spectroscopy.

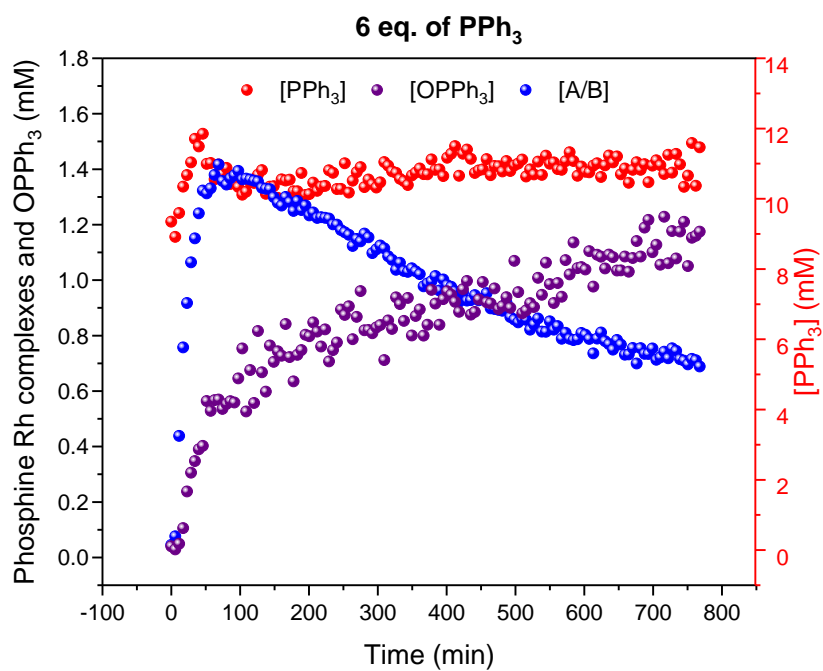


Figure S42. Concentration profiles for the reaction of **[2]** = 2.5 mM with 6 equivalents of PPh₃ in 22.4 mL of non-deuterated toluene under 10 bar of CO and H₂ at 50 °C as derived from quantitative FlowNMR spectroscopy.

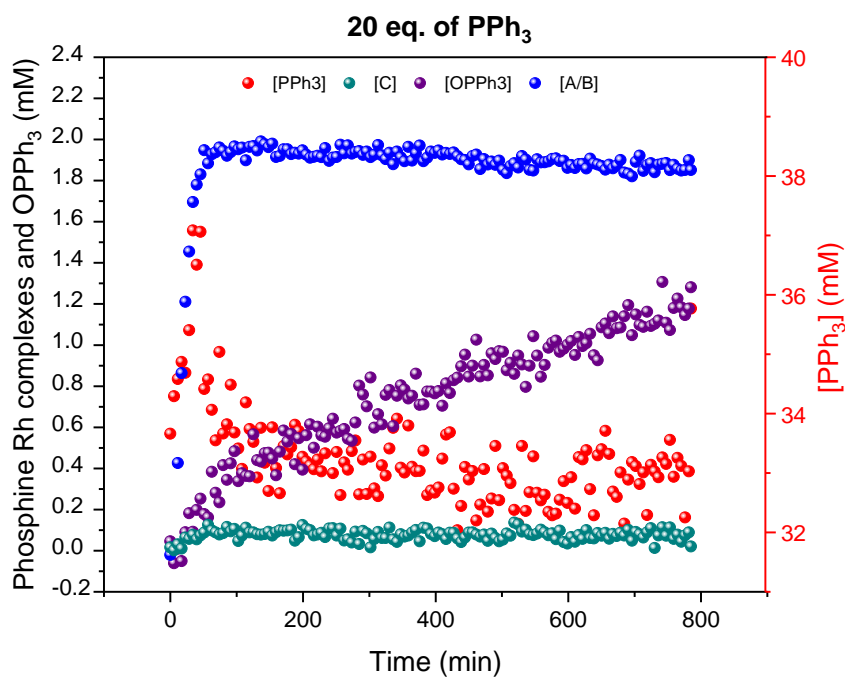


Figure S43. Concentration profiles for the reaction of **[2]** = 2.5 mM with 6 equivalents of PPh₃ in 22.4 mL of non-deuterated toluene under 10 bar of CO and H₂ at 50 °C as derived from quantitative FlowNMR spectroscopy.

³¹P{¹H} NMR

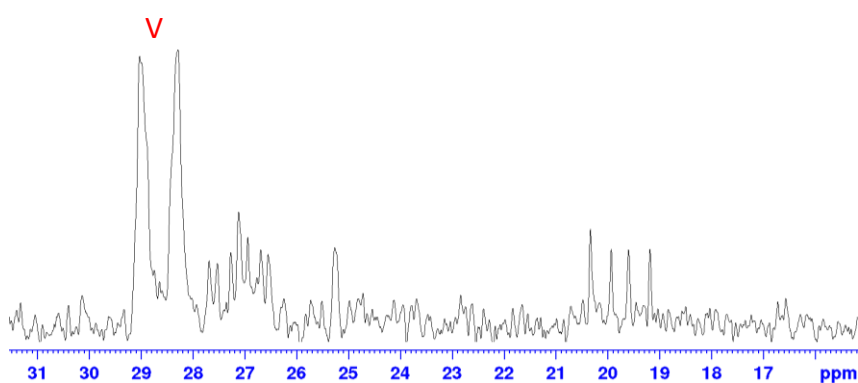


Figure S44. ³¹P{¹H} FlowNMR spectrum recorded of the reaction of **Y** (2.5 mM) with 1 equivalents of PPh₃ (2.5 mM) in 22.4 mL of non-deuterated toluene under 10 bar of CO and H₂ at -10 °C. The pump was stopped to keep the solution in the FlowNMR tip at the desired temperature.

$^{31}\text{P}\{^1\text{H}\}$ NMR

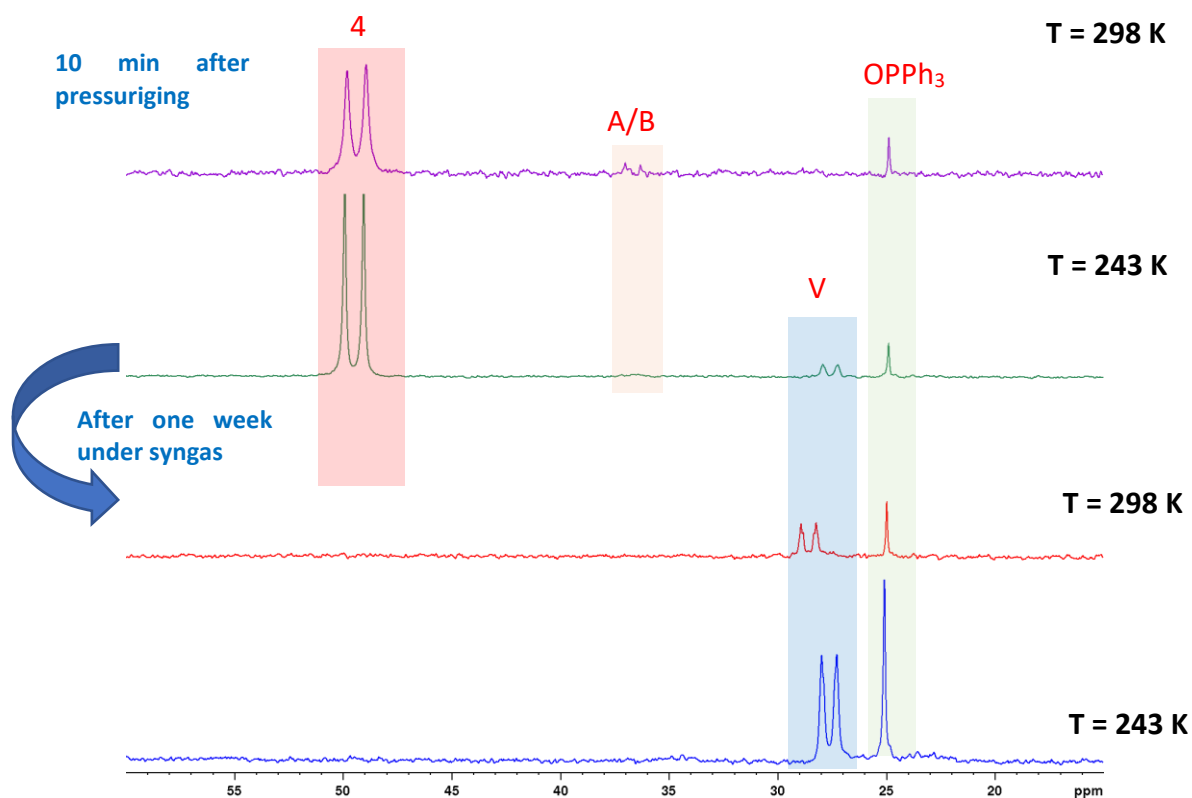


Figure S45. VT $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the mixture of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ (2.5 mM) in 0.8 mL of non-deuterated toluene under 5 bar of CO and H_2 after heating up to 50 °C recorded at 25 and -20 °C in a pressure NMR tube.

^1H NMR

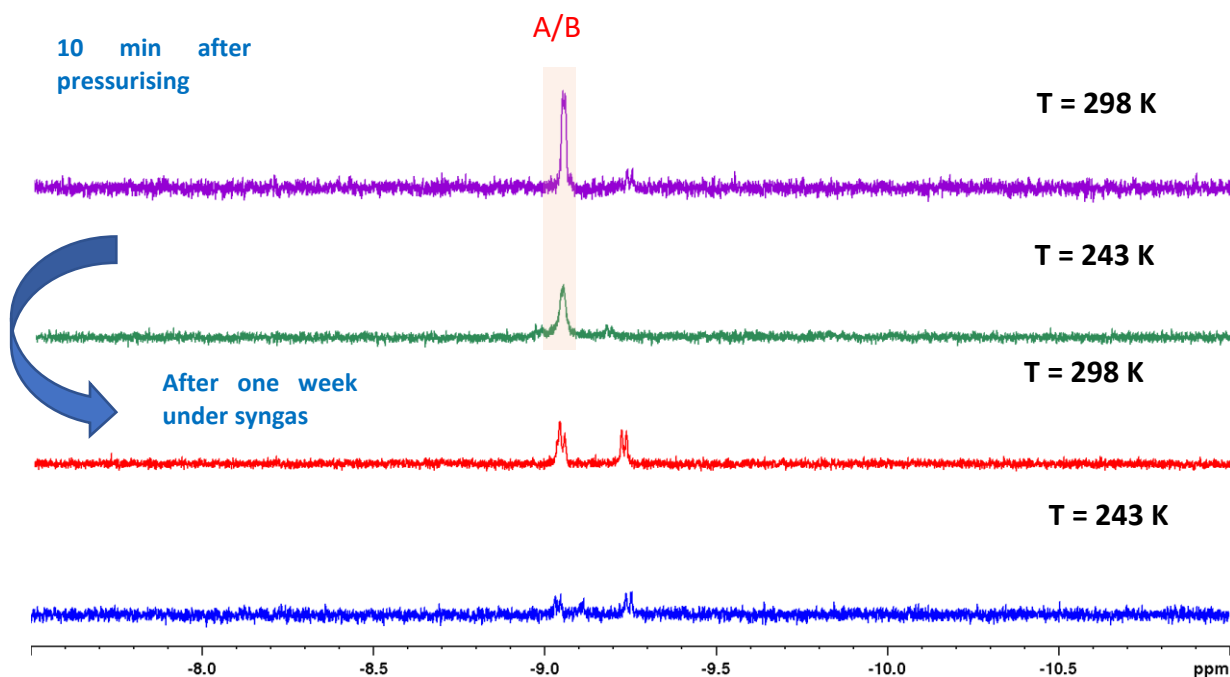


Figure S46. VT selective excitation ^1H NMR spectra of the mixture of $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ (2.5 mM) in 0.8 mL of non-deuterated toluene under 5 bar of CO and H_2 after heating up to 50 °C recorded at 25 and -20 °C in a pressure NMR tube.

$^{31}\text{P}\{^1\text{H}\}$ NMR

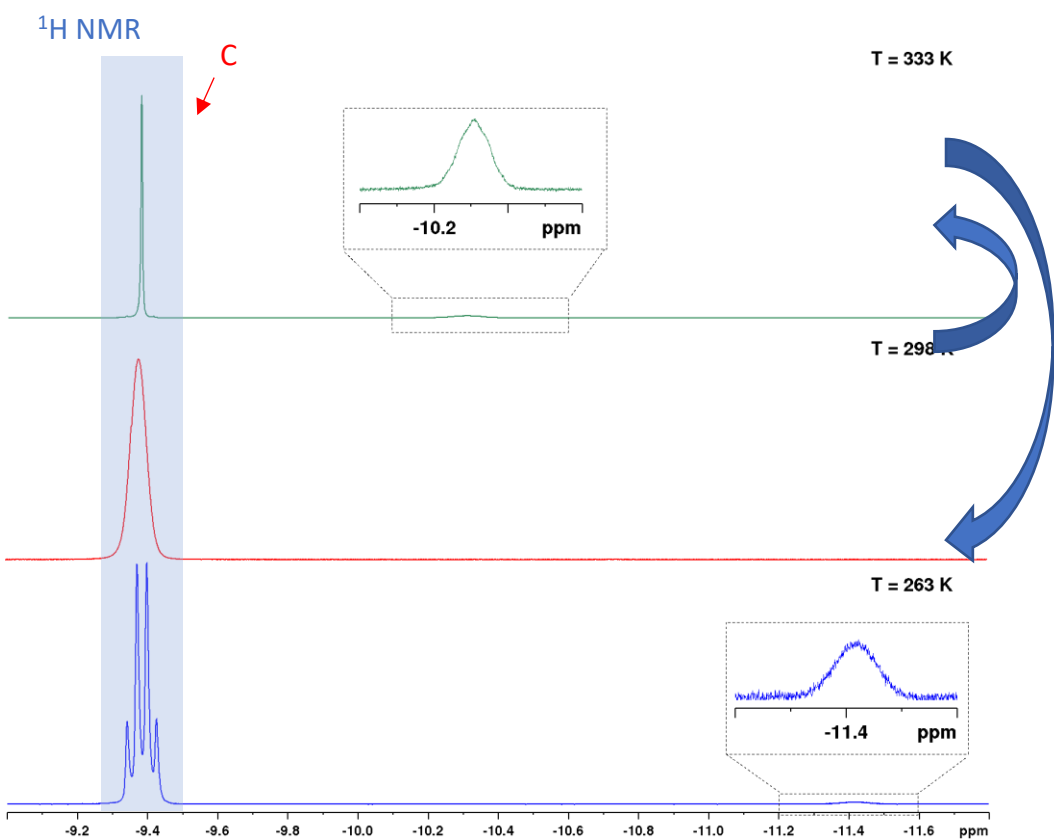
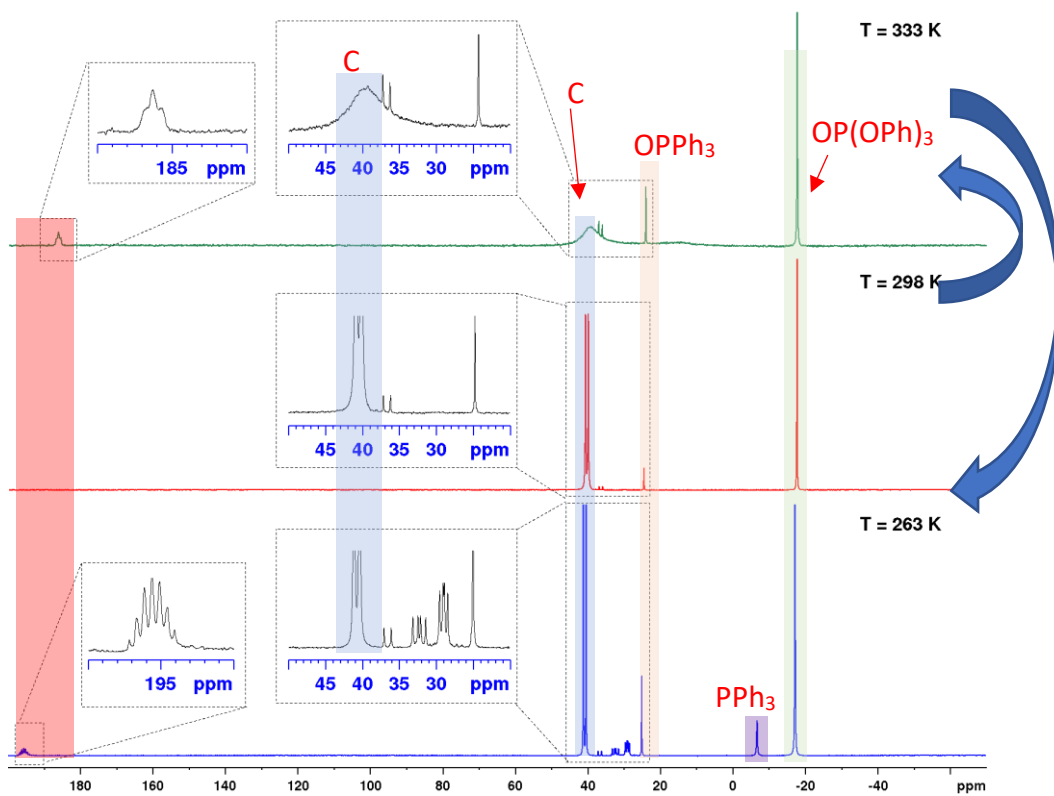


Figure S47. VT $^{31}\text{P}\{^1\text{H}\}$ and selective excitation ^1H NMR spectra of the thermal decomposition of **C** (2.5 mM) in the absence of added PPh_3 in 0.8 mL of non-deuterated toluene after heating the solution to 50 °C.

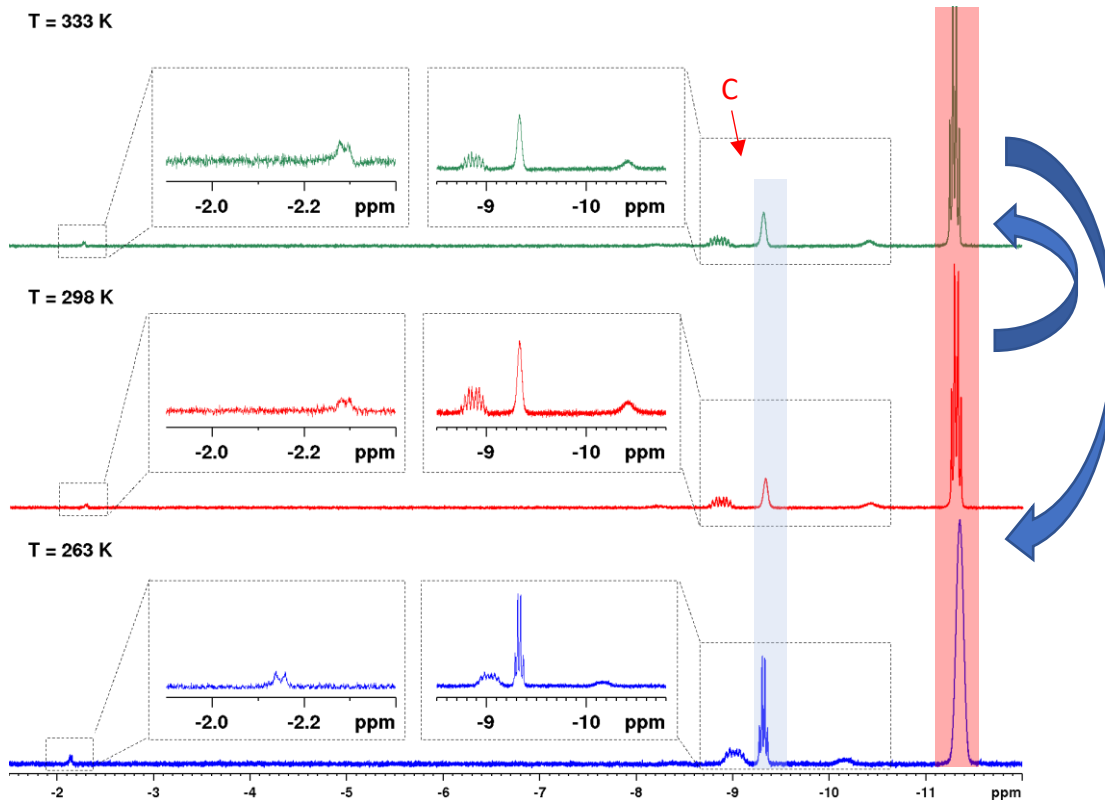
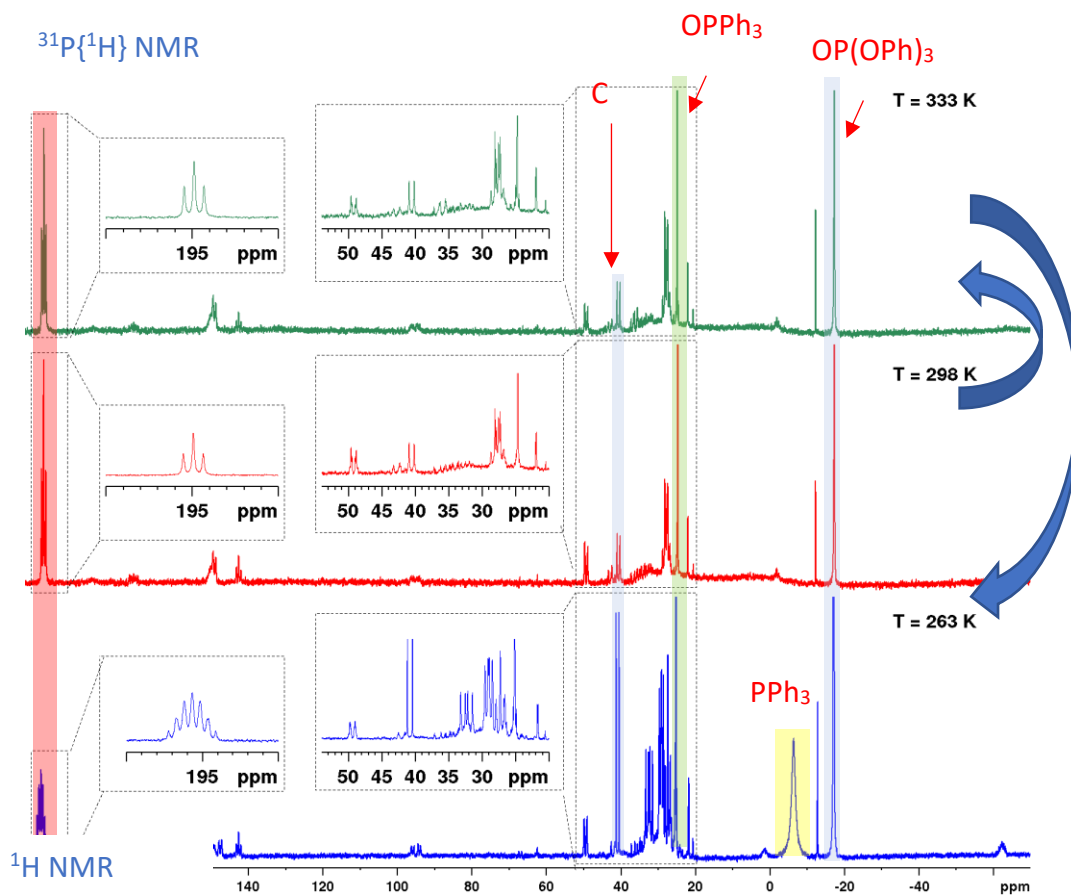


Figure S48. VT $^{31}\text{P}\{^1\text{H}\}$ and selective excitation ^1H NMR spectra of the thermal decomposition of **C** (2.5 mM) in the absence of added PPh₃ in 0.8 mL of non-deuterated toluene under Ar after heating the solution to 90 °C for one hour.

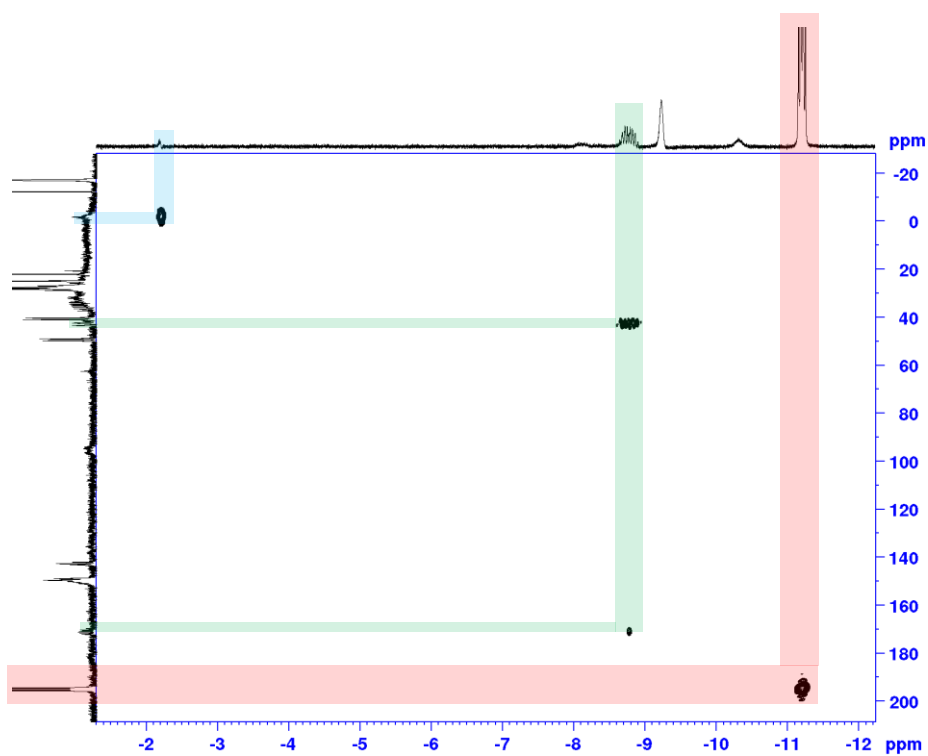


Figure S49. $^{31}\text{P}\{-^1\text{H}\}$ HMBC NMR spectrum recorded at 25 °C of **C** (2.5 mM) in 0.8 mL of non-deuterated toluene under Ar after heating the solution to 90 °C for one hour.

$^{31}\text{P}\{^1\text{H}\}$ NMR

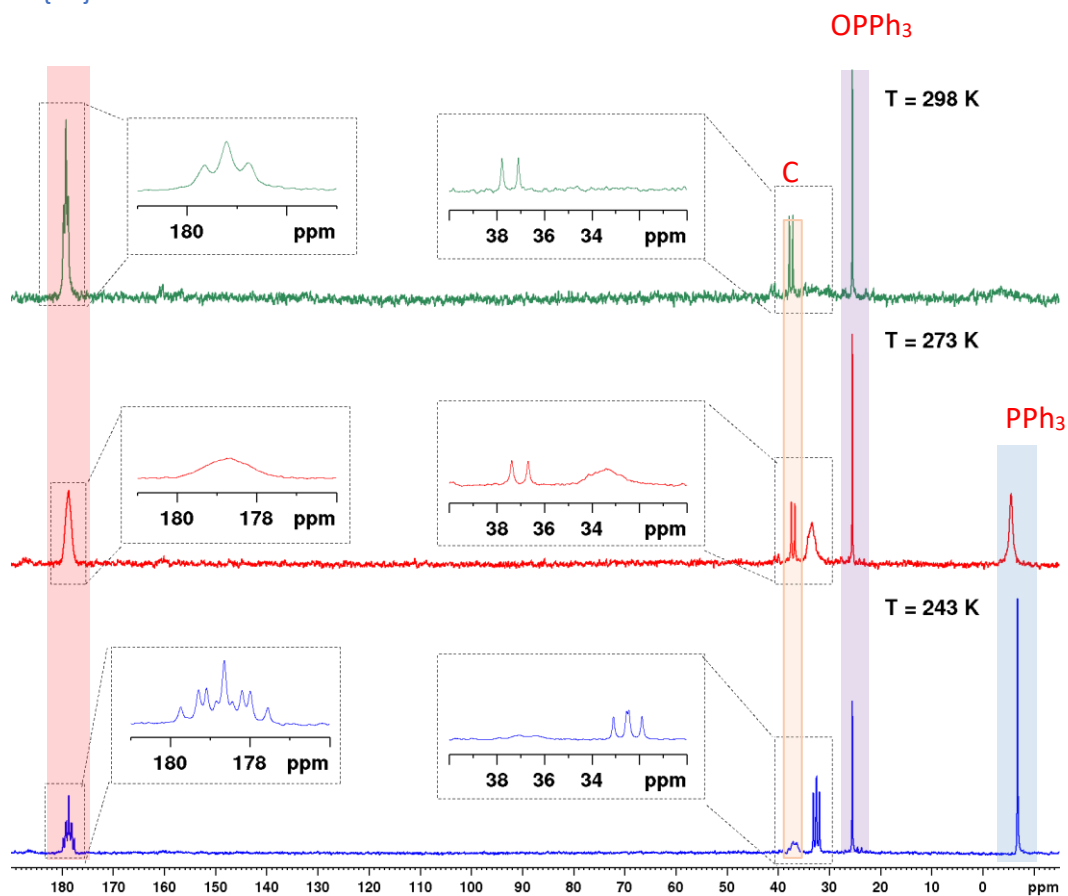


Figure S50. VT $^{31}\text{P}\{^1\text{H}\}$ spectra of the decomposition of **C** (2.5 mM) in the absence of added PPh_3 in 0.8 mL of non-deuterated toluene under 5 bar of CO and H_2 after heating the solution to 90 °C for one hour.

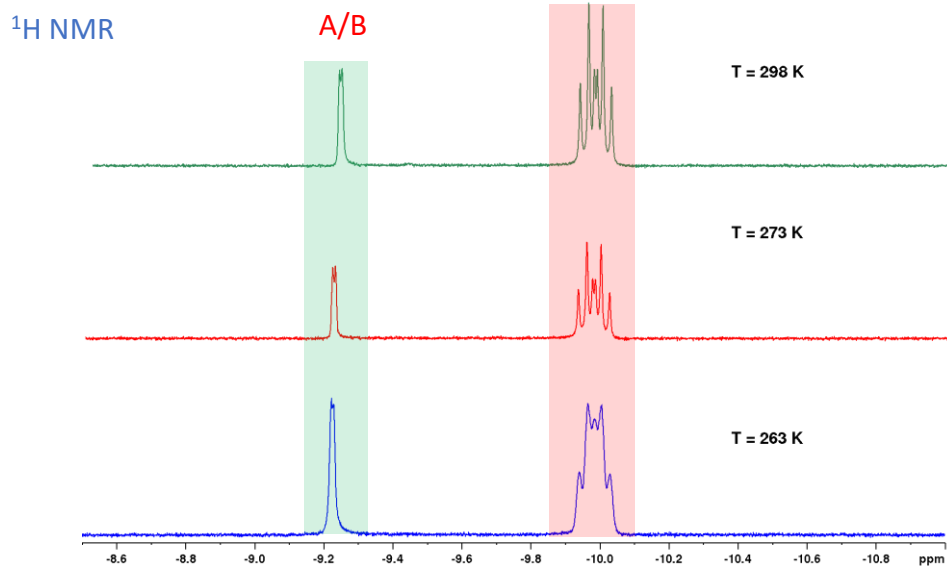


Figure S51. VT Selective excitation ¹H spectra of the thermal decomposition of C (2.5 mM) in the absence of added PPh₃ in 0.8 mL of non-deuterated toluene under 5 bar of CO and H₂ after heating the solution to 90 °C for one hour.

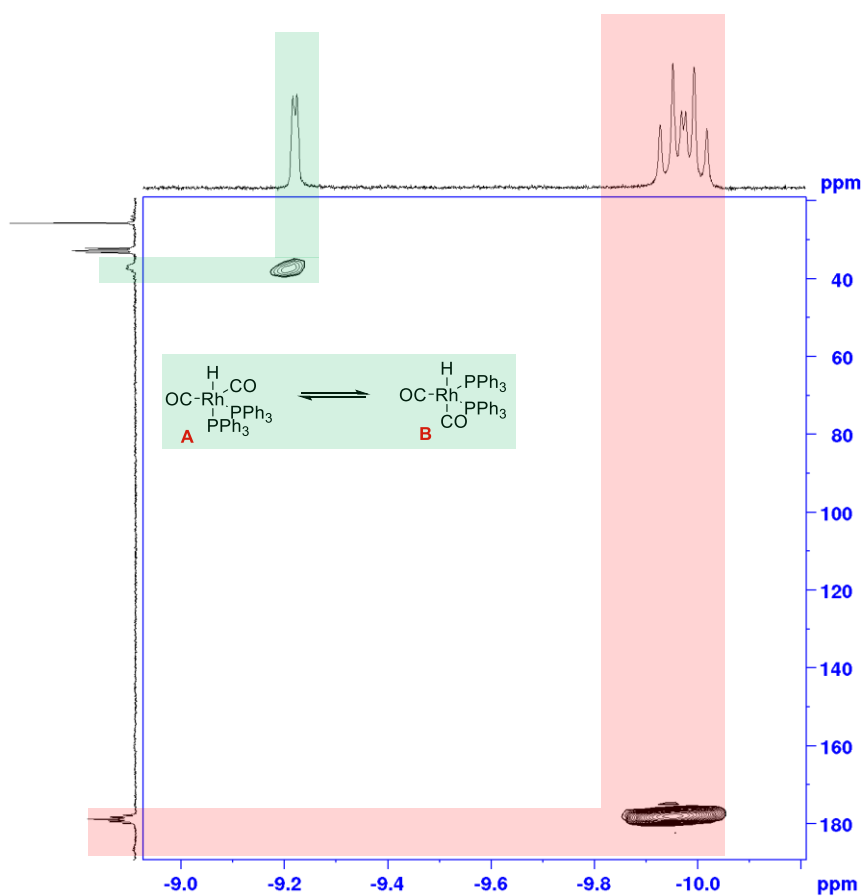


Figure S52. ¹H-³¹P HMBC NMR spectrum recorded at 25 °C of C (2.5 mM) in 0.8 mL of non-deuterated toluene under 5 bar of CO and H₂ after heating the solution to 90 °C for one hour.

$^{31}\text{P}\{^1\text{H}\}$ NMR

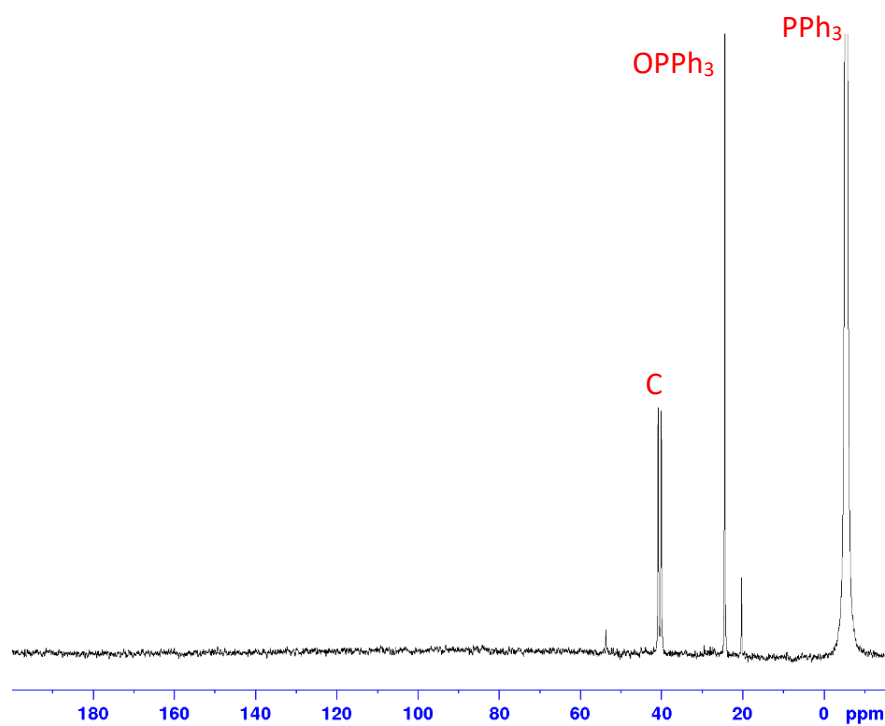


Figure S53. $^{31}\text{P}\{^1\text{H}\}$ spectrum of **C** (2.5 mM) with a large excess of PPh_3 (300 eq) in 0.8 mL of non-deuterated toluene under Ar recorded at 25° after heating the solution to 90 °C for one hour.

^1H NMR

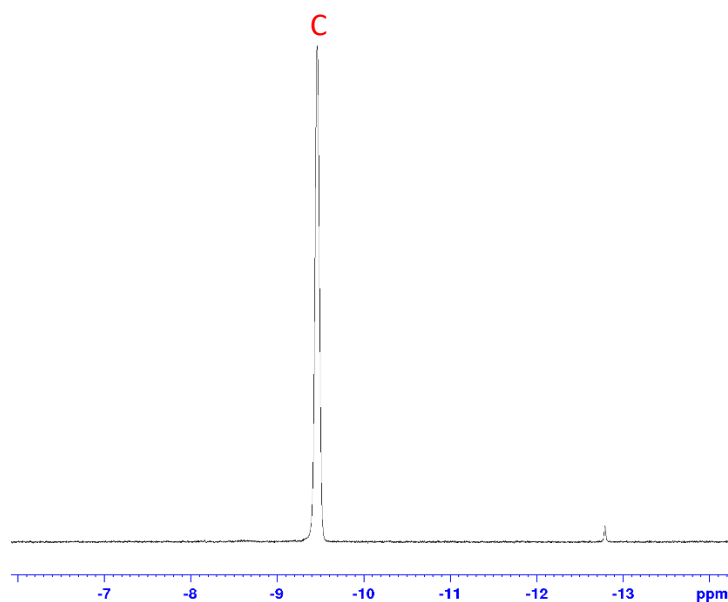


Figure S54. Selective excitation ^1H spectrum of **C** (2.5 mM) with a large excess of PPh_3 (300 eq.) in 0.8 mL of non-deuterated toluene recorded under Ar at 25° after heating the solution to 90 °C for one hour.

Table S5. Crystal data and structure for $[Rh(CO)_6(PPh_3)_2]$ (V).

Empirical formula	$C_{42} H_{30} O_6 P_2 Rh_2$	
Formula weight	898.42	
Temperature	150.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R-3	
Unit cell dimensions	$a = 15.22352(13)$ Å	$\alpha = 90^\circ$
	$b = 15.22352(13)$ Å	$\beta = 90^\circ$
	$c = 28.64224(17)$ Å	$\gamma = 120^\circ$
Volume	$5748.67(10)$ Å ³	
Z	6	
Density (calculated)	1.557 Mg/m ³	
Absorption coefficient	8.139 mm ⁻¹	
F(000)	2700	
Crystal size	0.160 x 0.084 x 0.074 mm ³	
Theta range for data collection	3.691 to 72.917°.	
Index ranges	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -35 ≤ l ≤ 24	
Reflections collected	27267	
Independent reflections	2545 [R(int) = 0.0289]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.64971	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2545 / 0 / 157	
Goodness-of-fit on F ²	1.070	
Final R indices [I > 2σ(I)]	R1 = 0.0168, wR2 = 0.0394	
R indices (all data)	R1 = 0.0175, wR2 = 0.0398	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.303 and -0.423 e.Å ⁻³	

5. References

- 1 M. Findeisen, T. Brand and S. Berger, *Magn. Reson. Chem.*, 2007, **45**, 175–178.