

## Following Palladium Catalyzed Methoxycarbonylation by Hyperpolarized NMR Spectroscopy: A Parahydrogen Based Investigation

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## Supporting Information

### 1. Experimental Section

**General Conditions.** All of the experimental procedures associated with this work were carried out under nitrogen using standard Schlenk techniques (with vacuum of up to  $10^{-2}$  mbar, with  $N_2$  or Ar as an inert atmosphere) or high vacuum techniques ( $10^{-4}$  mbar). Dry  $N_2$  and Ar for the Schlenk lines were purchased from BOC Gases. The solvents used were purchased as analytical grade from Fisher and dried using an Innovative Technology anhydrous solvent system, or distilled from an appropriate drying agent under nitrogen. The phosphine bcope was provided by Shell. The substrates Ph-C $\equiv$ C-Ph- $d_{10}$  and Ph- $^{13}C\equiv C$ -Ph- $d_{10}$ , and catalyst, were prepared according to literature methods with slight modification.[1] Methanol- $d_4$  was obtained from Sigma-Aldrich, and degassed before use. Dichloromethane- $d_2$  was bought from Sigma-Aldrich, dried and degassed by treating with  $CaH_2$  for 24 hours and transferred under high vacuum into a flame dried Schlenk flask. (E)-2,3-diphenylacrylic acid and AgOTf were obtained from Strem and Aldrich respectively and used as received.

**Instrumentation and preparation of NMR samples.** All NMR measurements were recorded on Bruker Avance III series 400 MHz or 500 MHz systems. NMR samples were prepared in 5 mm NMR tubes fitted with Young's valves. Each NMR sample contained  $\sim 1$  mg of catalyst and 2 mg of substrate. Samples were degassed 3 times under high vacuum prior to CO and  $p$ - $H_2$  (1:2 ratio and 3 bar in total) addition. The 1D and 2D NMR spectra were recorded using normal sequences to probe the emission signals or modified to use an initial  $\pi/4$  pulse when PHIP based magnetization was selected.[2]

**Synthesis of Pd(bcope)Cl $_2$ .** 350 mg (0.91 mmol) of [Pd(PhCN) $_2$ Cl $_2$ ] was dissolved in 10 mL of dry CH $_2$ Cl $_2$ , then a solution of bcope in CH $_2$ Cl $_2$  (312 mg, 1.00 mmol) added. The resulted solution was stirred for 2 hrs. After this time it was concentrated to ca. 1 mL and diethyl ether added (10 mL) to precipitate a solid which was washed with diethyl ether (3 x 2 mL) and dried under vacuum to give 345 mg of the title compound as a pale yellow solid. Percentage yield: 78 %.

**Synthesis of Pd(bcope)(OTf) $_2$ .** 345 mg (71 mmol) of Pd(bcope)Cl $_2$  was suspended in 30 ml of dry dichloromethane and 383 mg (1.49 mmol, 1.05 eq.) of AgOTf was added slowly. The resulting suspension was stirred at room temperature for 8 hours and filtered by cannula. The filtrate was pumped to dryness and a yellow solid collected, and subsequently recrystallized from methanol, to afford 525 mg of the title compound in a yield of 95 %.

**Generation of alternative precursor [Pd $_2$ (bcope) $_2$ (CO) $_2$ ](OTf) $_2$ .** A sample of **1** was dissolved in 0.6 ml of methanol- $d_4$ , the sample was degassed 3 times under high vacuum and then exposed to 1

bar of CO. The NMR tube was kept at 298 K and shaken occasionally for 12 hours, or until a  $^{31}\text{P}$  NMR spectrum indicated that the signal due to **1** at  $\delta$  74.0 was replaced by the signal due to  $[\text{Pd}_2(\text{bcope})_2(\text{CO})_2](\text{OTf})_2$  at ca.  $\delta$  50.0. This precursor was used without further purification.

**Synthesis of 6-OMe.** 1g of (E)-2,3-diphenylacrylic acid, 5 ml of methanol and 50 ml of toluene were placed in a 100 ml flask. 1 ml of concentrated  $\text{H}_2\text{SO}_4$  was then added. The resulting clear solution was heated to reflux for 8 hours. The solution was then washed with 10 ml of water saturated with NaCl, dried over  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The crude product was then recrystallized in methanol to yield 0.95 g of a white powder in a yield of 92 %.

**GC/MS analysis.** GC/MS data studies were performed on a Varian SATURN GC/MS 2000 gas chromatograph coupled to a mass spectrometer detector. A Factor-Form<sup>TM</sup> VF-6mg capillary column (30 m x 0.25 mm ID and 0.25  $\mu\text{m}$  film thickness) was used for GC separation. The initial oven temperature was 100  $^\circ\text{C}$ , the temperature was then raised from 100 to 145  $^\circ\text{C}$  at 2.5 K/min, and from there to 250  $^\circ\text{C}$  at 30 K/min, with the maximum temperature being held for 50 min. Helium was used as the carrier gas (flow rate 1.0 mL/min). Mass spectra were recorded in the EI mode (70 eV) on the 30-650  $m/z$  range.

For the GC/MS measurements, a methanol solution (1 mL) of the palladium complex (ca. 1 mg) and diphenylacetylene (ca. 10 fold excess, 2 mg) was degassed and placed under  $\text{CO}/\text{H}_2$  atmosphere (3 atm). The mixture was heated at 323 K and monitored after 1h (the sample was shaken every 15 min to mimic the NMR conditions). In order to obtain a relative response factor for the different species formed in this reaction, a control sample containing known amounts of diphenylacetylene, *cis*-stilbene, *trans*-stilbene and 1, 2-diphenylethane in methanol was analyzed.

**EXSY measurements.** A series of exchange spectroscopy (EXSY) measurements were made to probe the dynamic behavior of these systems. This process involved the selective excitation of a single resonance and the subsequent measurement of a  $^1\text{H}$  NMR spectrum at time,  $t$ , after the initial pulse. The resulting measurements consisted of a series of data arrays such that  $t$  is varied between 10 and 25 values, typically between 0.1 to 1.0 s, to encode the reaction profile. The precise values were varied with temperature to suit the speed of the process. Data was collected for a range of temperatures and sample concentrations. Integrals for the interchanging peaks in the associated  $^1\text{H}$  EXSY spectra were obtained and converted into a percentage of the total detected signal (see section 3.0).

## 2. NMR characterization data for reaction intermediates and products

### 2.1 NMR information for Pd(bcope)(OTf)<sub>2</sub> (**1**)

The NMR and XRD characterisation of **1** have been reported previously. The identity of **1** was confirmed by comparison.[1] (CDCl<sub>3</sub>, 298 K): <sup>31</sup>P: δ 74.0

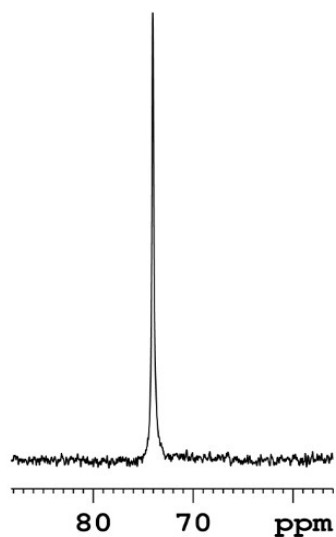


Figure S-1: The 1D <sup>31</sup>P NMR spectrum of Pd(bcope)(OTf)<sub>2</sub>

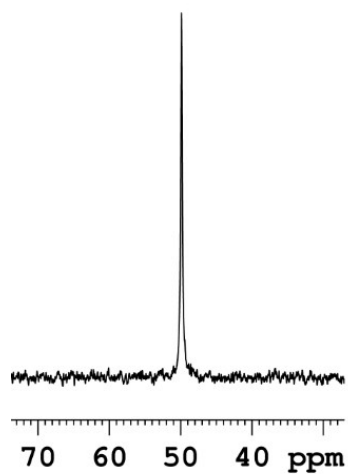
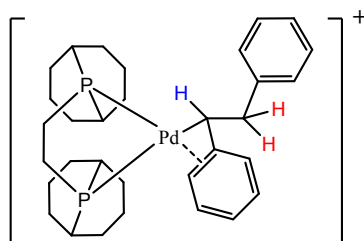


Figure S-2: The *in-situ* 1D <sup>31</sup>P NMR spectrum of [Pd<sub>2</sub>(bcope)<sub>2</sub>(CO)<sub>2</sub>](OTf)<sub>2</sub>

## 2.2 NMR information for [Pd(CHPhCH<sub>2</sub>Ph)(bcope)](OTf) (**2**)



The characterization of **2** has been reported previously, its identity was confirmed by comparing key NMR data with that published.[1] (CD<sub>2</sub>Cl<sub>2</sub>, 313 K) <sup>1</sup>H: δ 4.95 (m, J<sub>HH</sub> = -4.3 Hz, 11.2 Hz, CHPh), δ 3.10 (dd, CH<sub>2</sub>Ph, J<sub>HH</sub> = -4.3 Hz, 15.0 Hz) and δ 2.93 (dd, CH<sub>2</sub>Ph, J<sub>HH</sub> = 11.2, 15.0 Hz); <sup>31</sup>P{<sup>1</sup>H}: δ 32.2 (d, J<sub>PP</sub> = 90.2 Hz, P *trans* to alkyl), δ 42.1 (d, J<sub>PP</sub> = 90.2 Hz, P *cis* to alkyl); <sup>13</sup>C{<sup>1</sup>H}: δ 35.2 (dd, J<sub>CP</sub> = 16.2 Hz, 5.4 Hz, CH<sub>2</sub>Ph), δ 62.3 (dd, J<sub>CP</sub> = 54.0 Hz, 16.2 Hz, CHPh).

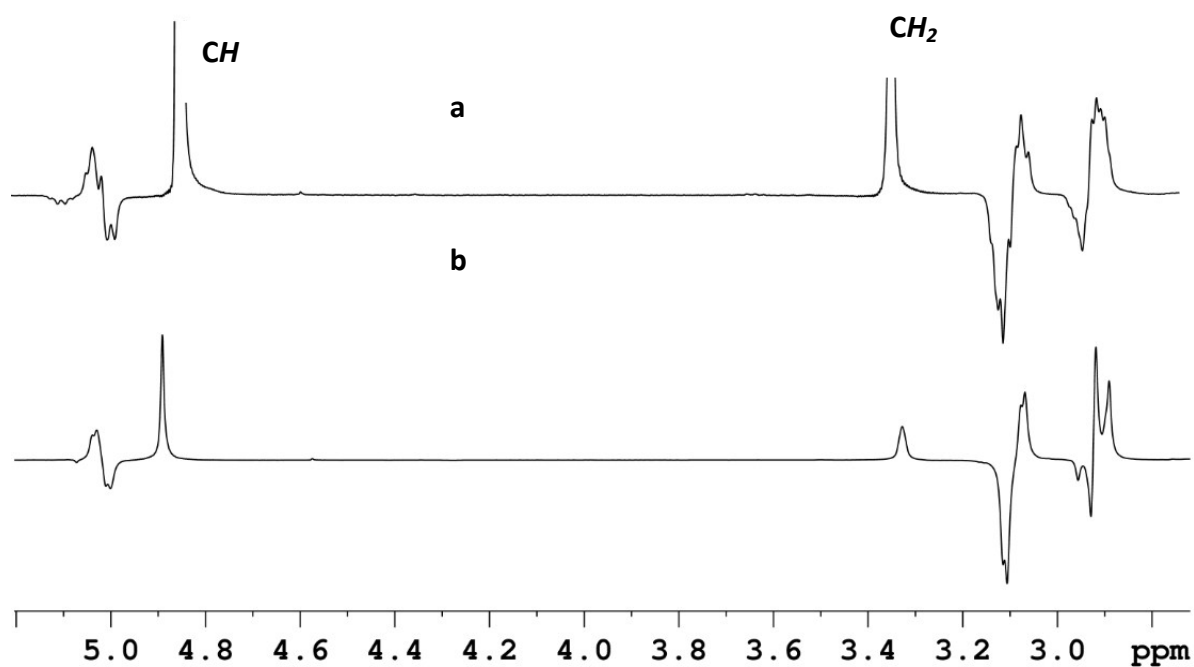
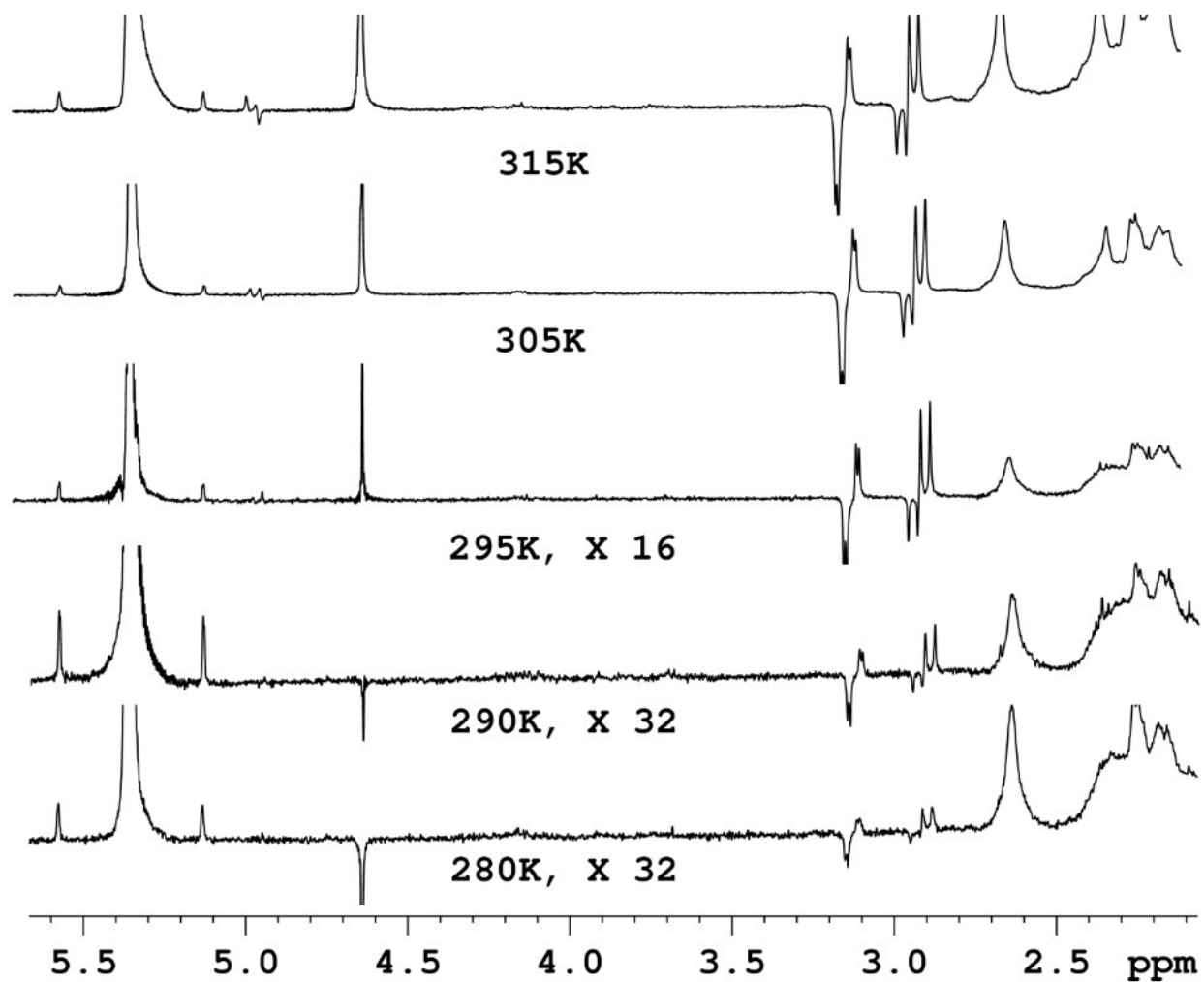
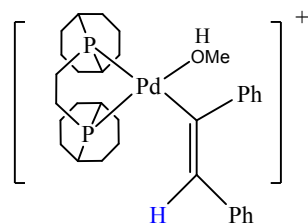


Figure S-3: Typical 1D <sup>1</sup>H NMR spectra of **2a** in methanol-*d*<sub>4</sub> at 323 K: a): <sup>1</sup>H; b): <sup>1</sup>H{<sup>31</sup>P}



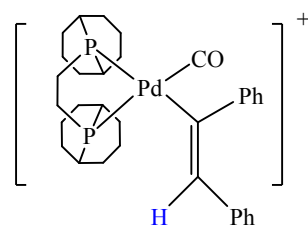
**Figure S-4:**  $^1\text{H}\{^{31}\text{P}\}$  NMR spectra, at the indicated temperatures, showing the temperature dependence of intensities of different protons exhibited by complex 2 under PHIP. The emission peak seen for  $\text{H}_2$  indicates its exchange with other active species.

### 2.3 NMR information for [Pd(CPh=CHPh)(bcope)(CD<sub>3</sub>OD)](OTf) (3-CD<sub>3</sub>OD)



The NMR characterisation of **3-CD<sub>3</sub>OD** has been reported previously. Its identity was confirmed by comparing its NMR data with that reported.[1] (CD<sub>3</sub>OD, 313 K) <sup>1</sup>H: δ 6.77 (dd, J<sub>PH</sub> = 13.6 Hz, 6.8 Hz, 1H, *CHPh*); <sup>31</sup>P {<sup>1</sup>H}: δ 21.8 (m, J<sub>PH</sub> = 13.6 Hz, P *trans* to vinyl), 39.0 (m, J<sub>PH</sub> = 6.8 Hz, P *cis* to vinyl).

### 2.4 NMR information for [Pd(CPh=CHPh)(bcope)(CO)](OTf) (3-CO)



(CD<sub>3</sub>OD, 308 K); <sup>1</sup>H: δ 6.90 (br, 1H, *PhCH*).

**Effect of the catalyst/CO ratio dependence on the formation of 3-CO.** This study was achieved by dissolving different amounts of precursor **1** and 12 mg of diphenyl acetylene, in methanol-*d*<sub>4</sub>. The sample was then degassed and exposed to a mixture of CO/H<sub>2</sub>. NMR spectra were then recorded at 313 K.

**Table S-1: Reaction conditions used to study the impact of catalyst/CO ratio during the diphenyl acetylene carbonylation**

Entry	Catalyst	solvent	substrate	CO	<i>p</i> -H <sub>2</sub>	Total
a	6mg	0.6 ml	6 mg	1 atm.	2 atm.	3 atm.
b	3mg	0.6 ml	6 mg	1 atm.	2 atm.	3 atm.
c	1.5mg	0.6 ml	6 mg	1 atm.	2 atm.	3 atm.

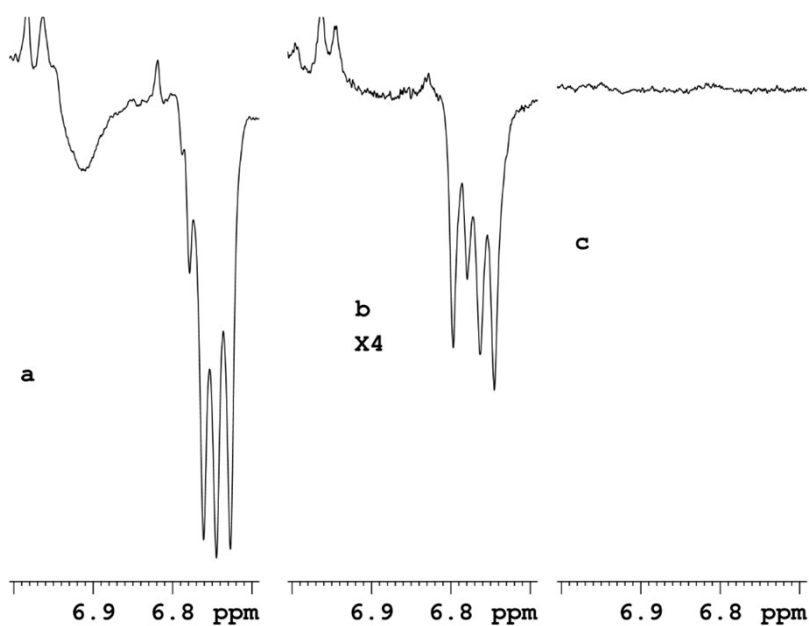
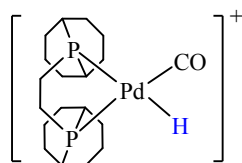


Figure S-5:  $^1\text{H}\{^{31}\text{P}\}$  NMR spectra showing the dependence in intensity of the vinyl proton signal of 3-CO and 3- $\text{CD}_3\text{OD}$  with *parahydrogen* and carbon monoxide ratio.

## 2.5 NMR information for $[\text{PdH}(\text{bcope})(\text{CO})](\text{OTf})$ (4-CO)



( $\text{CD}_2\text{Cl}_2$ , 313 K);  $^1\text{H}$ :  $\delta$   $-4.64$  (dd,  $J_{\text{PH}} = 190.0$  Hz,  $29.0$  Hz, hydride);  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$   $46.0$  (d,  $J_{\text{PH}} = 190.0$  Hz, P *trans* to hydride).

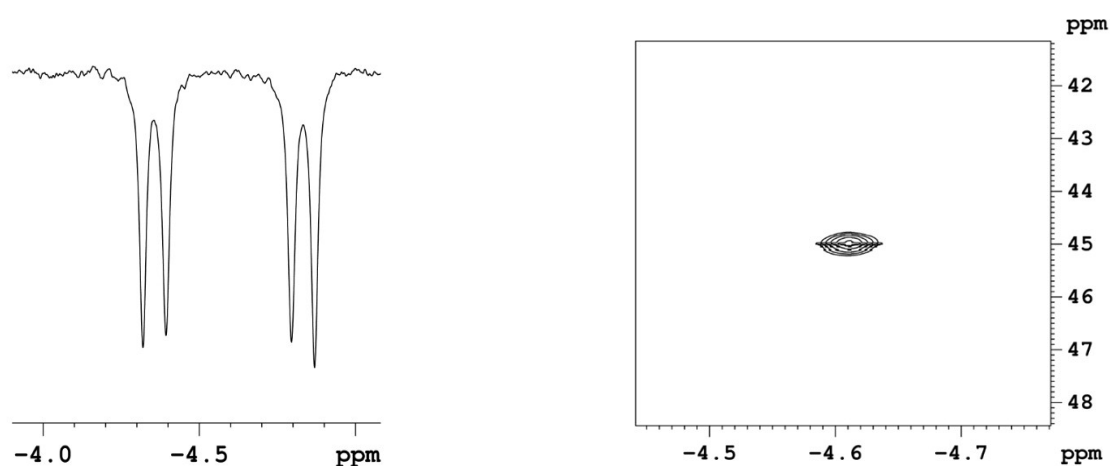
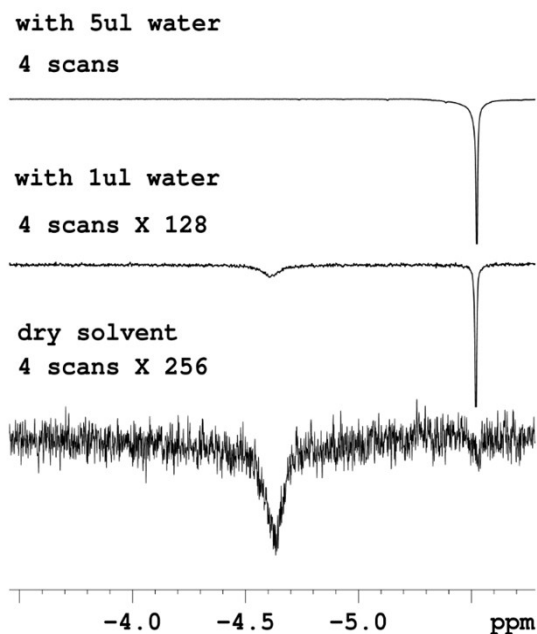


Figure-S6: Full coupled hydride signal for 4-CO

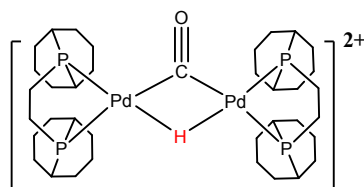
Figure-S7: 2D  $^1\text{H}$ - $^{31}\text{P}$  HMQC NMR spectrum showing the correlation between the *trans* hydride signal and phosphorus center of 4-CO.





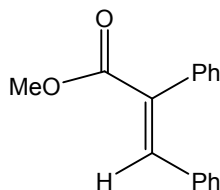
**Fig-S8: (left) three  $^1\text{H}\{^{31}\text{P}\}$  NMR spectra that show the impact of water during diphenyl acetylene carbonylation: a): with 5 $\mu\text{l}$   $\text{H}_2\text{O}$  added; b): with 1 $\mu\text{l}$  of  $\text{D}_2\text{O}$  added, c): no water added, and the solvent dried over  $\text{CaH}_2$  and transferred into the NMR tube under vacuum.**

## 2.6 NMR information for $[(\text{bcope})\text{Pd}(\mu\text{-H})(\mu\text{-CO})\text{Pd}(\text{bcope})][\text{OTf}]$ (**5**)



The NMR characterization of compound **5** has been reported previously. Its identity was confirmed by comparing key NMR data with those reported results. ( $\text{CD}_3\text{OD}$ , 308 K)  $^1\text{H}$ : -5.34 (quint,  $J_{\text{PH}} = 47.2$  Hz, 1H, hydride);  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  -20.9 (d,  $J_{\text{PH}} = 47.2$  Hz).

## 2.7 NMR information for PhHC=C(Ph)COOMe (6-OMe)



(CDCl<sub>3</sub>, 298 K): <sup>1</sup>H: δ 7.84 (s, 1H, *CHPh*, <sup>1</sup>J<sub>CH</sub> = 156.0 Hz, <sup>2</sup>J<sub>CH</sub> = 3.5 Hz; <sup>3</sup>J<sub>CH</sub> = 7.5 Hz), δ 3.82 (s, 3H, OCH<sub>3</sub>), δ 7.06 (t, 2H, J<sub>HH</sub> = 7.5 Hz, *o*-H of *PhC*), δ 7.18 (t, 2H, J<sub>HH</sub> = 7.5 Hz, *m*-H of =*PhC*), δ 7.65 (t, 1H, J<sub>HH</sub> = 7.5 Hz, *p*-H of *PhCH*), δ 7.21 (t, 2H, J<sub>HH</sub> = 7.5 Hz, *o*-H of *PhC*), δ 7.38 (t, 2H, J<sub>HH</sub> = 7.5 Hz, *m*-H of *PhCH*), δ 7.52 (t, 1H, J<sub>HH</sub> = 7.5 Hz *p*-H of =*PhCH*); <sup>13</sup>C{<sup>1</sup>H}: δ 140.5 (s, 1H, <sup>1</sup>J<sub>CH</sub> = 156.0 Hz, *CHPh*), δ 132.6 (s, 1H, <sup>2</sup>J<sub>CH</sub> = 3.6 Hz, *CPh*), δ 168.0 (s, 1H, <sup>3</sup>J<sub>CH</sub> = 7.5 Hz, C=O), δ 130.6, 129.8 (*CPh*), δ 129.1, 127.9, δ 126.7 (*CHPh*).

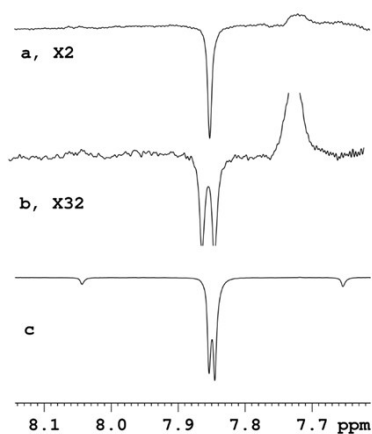


Figure S-9: Shape of the vinyl proton signal of 6 under the specified conditions: a): normal; b): with <sup>13</sup>CO; c): with Ph<sup>13</sup>CCPh. All spectra recorded at 323 K in methanol-*d*<sub>4</sub>

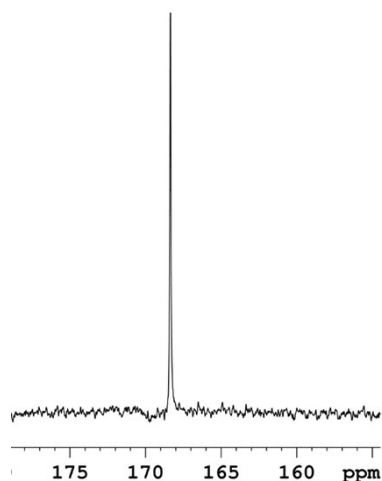


Figure S-10: <sup>13</sup>C NMR spectrum showing that 6 is the only CO containing products

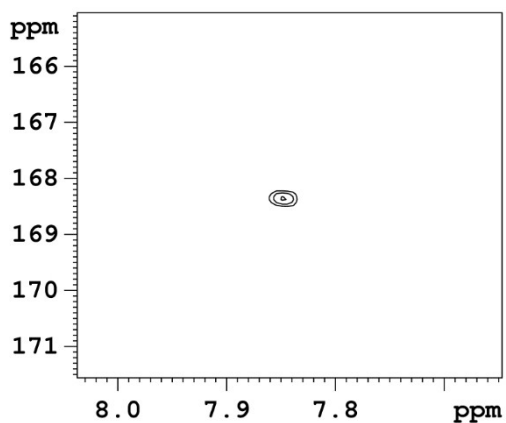
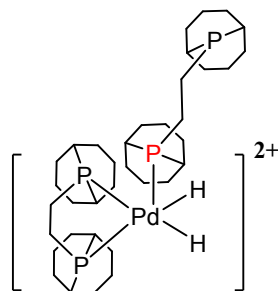
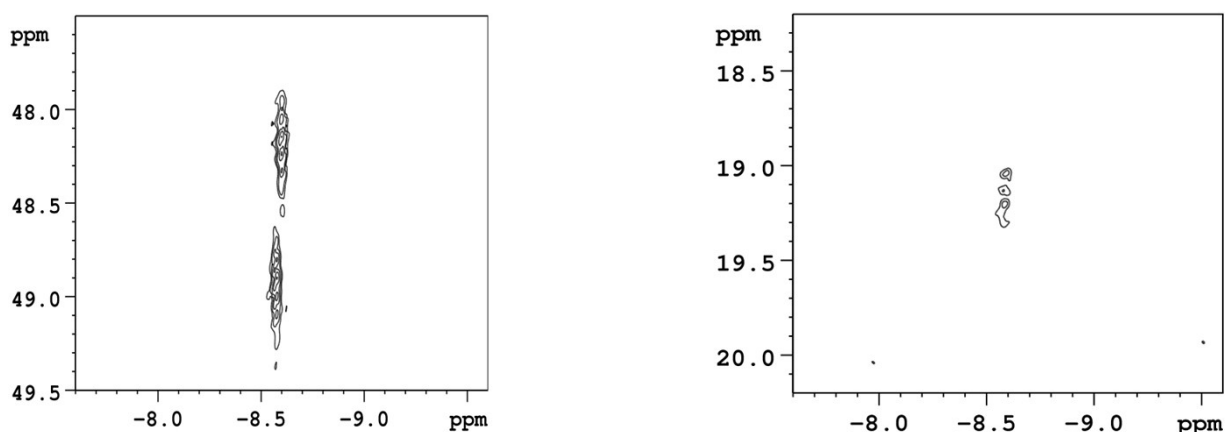


Figure S-11: (left) 2D <sup>1</sup>H-<sup>13</sup>C HMQC NMR spectrum showing the correlation between the vinyl proton signal and the carbonyl group in 6

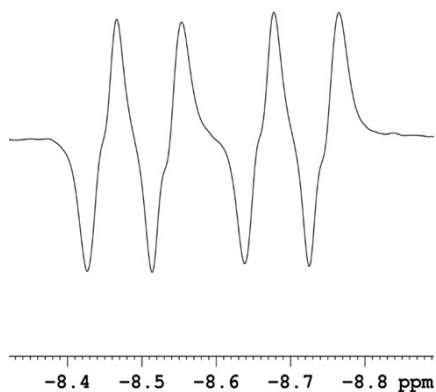
## 2.8 NMR information for $[\text{Pd}(\text{H})_2(\mu^1\text{-bcope})(\mu^2\text{-bcope})][\text{OTf}]$ (7)



( $\text{CD}_3\text{OD}$ , 308 K)  $^1\text{H}$ :  $\delta$  -8.59 (ddt,  $J_{\text{PH}} = 105.4$  Hz, 44.2 Hz, 10 Hz,  $J_{\text{HH}} = -10$  Hz, hydride a),  $\delta$  -8.61 (ddt,  $J_{\text{PH}} = 105.4$  Hz, 44.2 Hz, 10 Hz,  $J_{\text{HH}} = -10$  Hz, hydride b);  $^{31}\text{P}\{^1\text{H}\}$ :  $\delta$  48.9 (m,  $J_{\text{PH}} = 105.4$  Hz, 44.2 Hz,  $J_{\text{PP}} = 29.4$  and 12.6 Hz, P *trans* to hydride a),  $\delta$  48.2 (m,  $J_{\text{PH}} = 105.4$  Hz, 44.2 Hz,  $J_{\text{PP}} = 29.4$  and 12.6 Hz, P *trans* to hydride b), 19.2 (t,  $J_{\text{PH}} = 10$  Hz,  $J_{\text{PP}} = 12.6$  Hz).

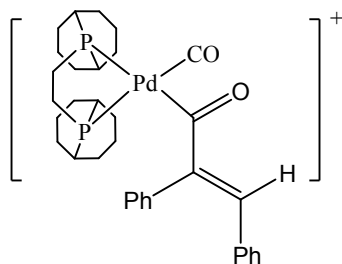


**Figure S-12: 2D  $^1\text{H}$ - $^{31}\text{P}$  HMQC NMR spectrum showing the correlation connecting the two hydride signals of 7 with its phosphorus centers: (left): The two hydride signals and 2 phosphorus centers that are *trans* to each other. (right) The hydride signals and the capping phosphorus center**



**Figure S-13: Fully coupled  $^1\text{H}$  NMR spectrum showing the hydride signals due to 7.**

## 2.9 NMR information for [Pd(-CO-C(Ph)=CHPh(bcope)(CO)](OTf) (8)



[Pd(-CO-C(Ph)=CHPh(bcope)(CO)](OTf) (**8**) (CD<sub>2</sub>Cl<sub>2</sub>, 313 K) <sup>1</sup>H NMR: δ 7.89 (dd, J<sub>PH</sub> = 22.0 Hz, 3.5 Hz, <sup>1</sup>J<sub>CH</sub> = 156.2 Hz, <sup>2</sup>J<sub>CH</sub> = 3.5 Hz, 1H, vinyl H); <sup>31</sup>P{<sup>1</sup>H}: δ 36.0, (m, J<sub>PH</sub> = 22.2 Hz, P *trans* to vinyl), δ 43.2, (m, J<sub>PH</sub> = 3.5 Hz, P *cis* to vinyl); <sup>13</sup>C{<sup>1</sup>H}: δ 137.2 (d, J<sub>CH</sub> = 156.2 Hz, CHPh), δ 137.8 (d, J<sub>CH</sub> = 3.4 Hz, CPh).

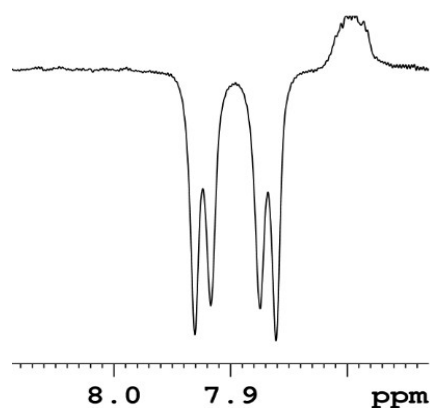


Figure S-14: Selected expansion showing the vinyl proton signal of **8** in a fully coupled <sup>1</sup>H NMR spectrum

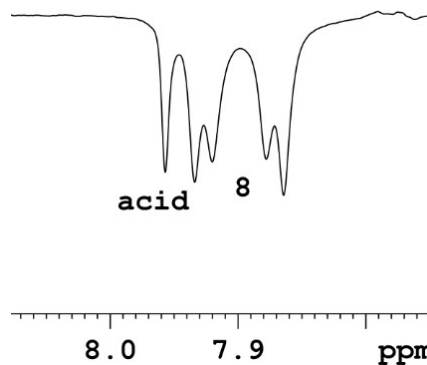


Figure S-15: Selected expansion of the vinyl proton due to **8** and the corresponding acid signal detected when 1 μl of water is added to the DCM sample

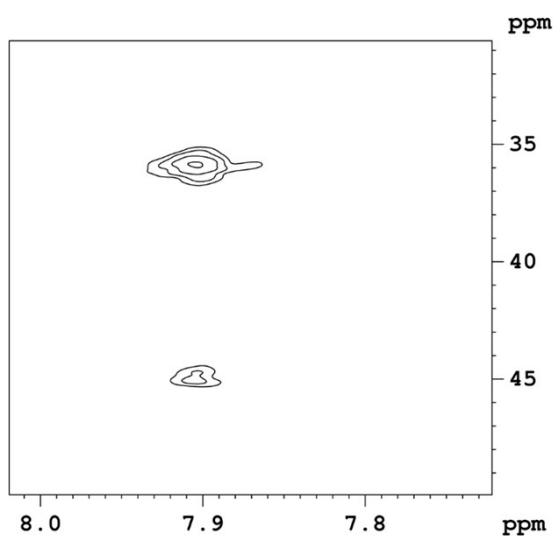


Figure S-16: 2D <sup>1</sup>H-<sup>31</sup>P HMQC NMR spectrum showing the correlation between the vinyl proton signal and the two phosphorus centers of **8**

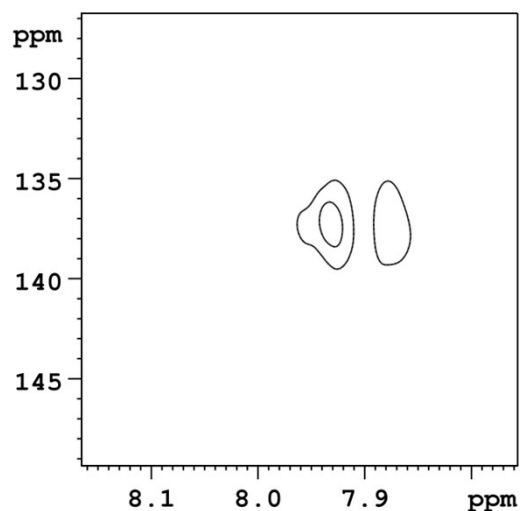
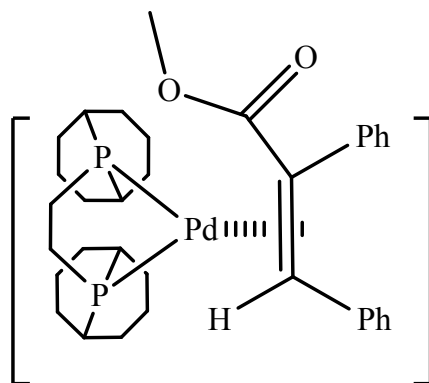


Figure S-17: 2D <sup>1</sup>H-<sup>13</sup>C HMQC NMR spectrum showing the correlation between the vinyl proton signal of **8** and the carbon centre it attaches to.

## 2.10 NMR information for [Pd(MeOOCPhC=CHPh)(bcope)] (9)



(CD<sub>3</sub>OD, 333 K) <sup>1</sup>H: δ 5.08 (m, J<sub>PH</sub>=7.0 Hz, <sup>3</sup>J<sub>CH</sub> = 7.5 Hz, PhCH).

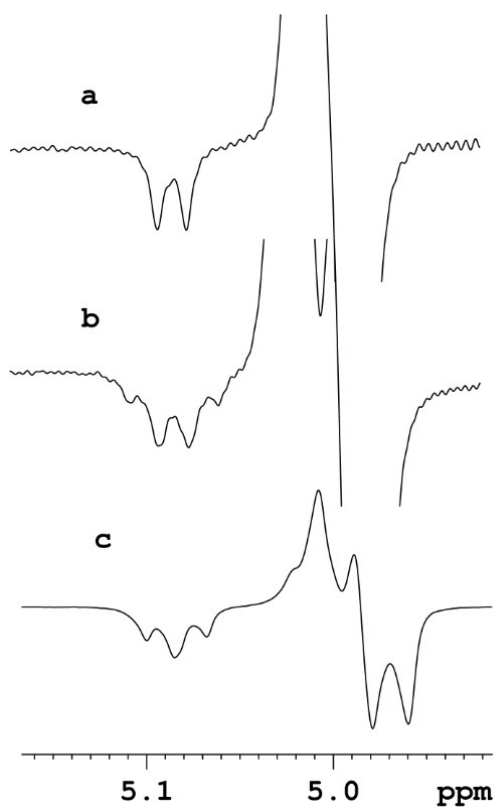
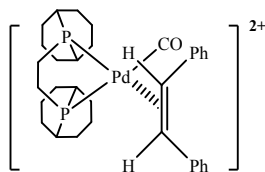
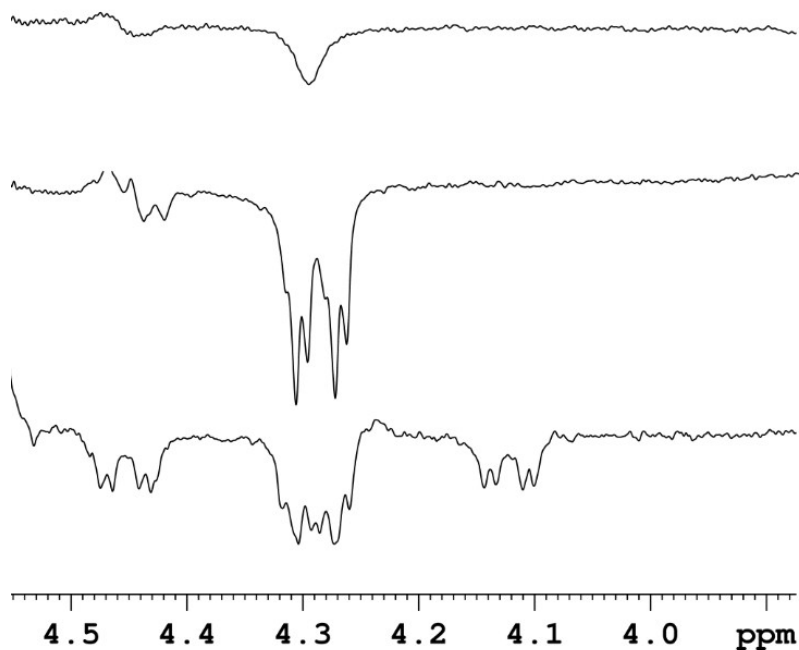


Fig-S18: Expansion of a series of <sup>1</sup>H NMR spectra showing the vinyl proton signal of 9, at δ 5.08, under the specified conditions: a): <sup>1</sup>H{<sup>31</sup>P}, with <sup>13</sup>CO, at 308 K; b): <sup>1</sup>H, with <sup>13</sup>CO, at 308 K; c): <sup>1</sup>H{<sup>13</sup>C}, using normal CO, at 313 K

## 2.11 NMR information for [Pd(*cis*-PhCH=CHPh)](bcope)(CO).2(OTf) (10)

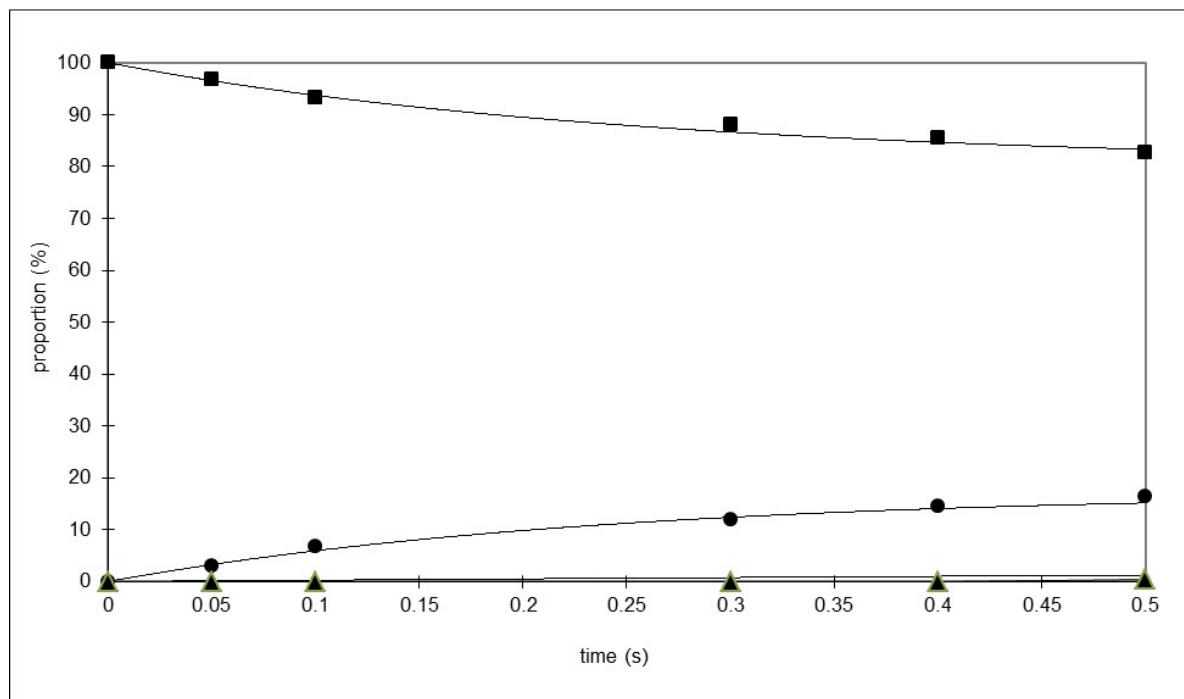


(CD<sub>3</sub>OD, 333 K) <sup>1</sup>H: δ 4.26 (m, J<sub>PH</sub>=13.0 Hz, 3.7 Hz, <sup>1</sup>J<sub>CH</sub> = 133.5 Hz, <sup>2</sup>J<sub>CH</sub> = 3.3 Hz, PhCH=CHPh).



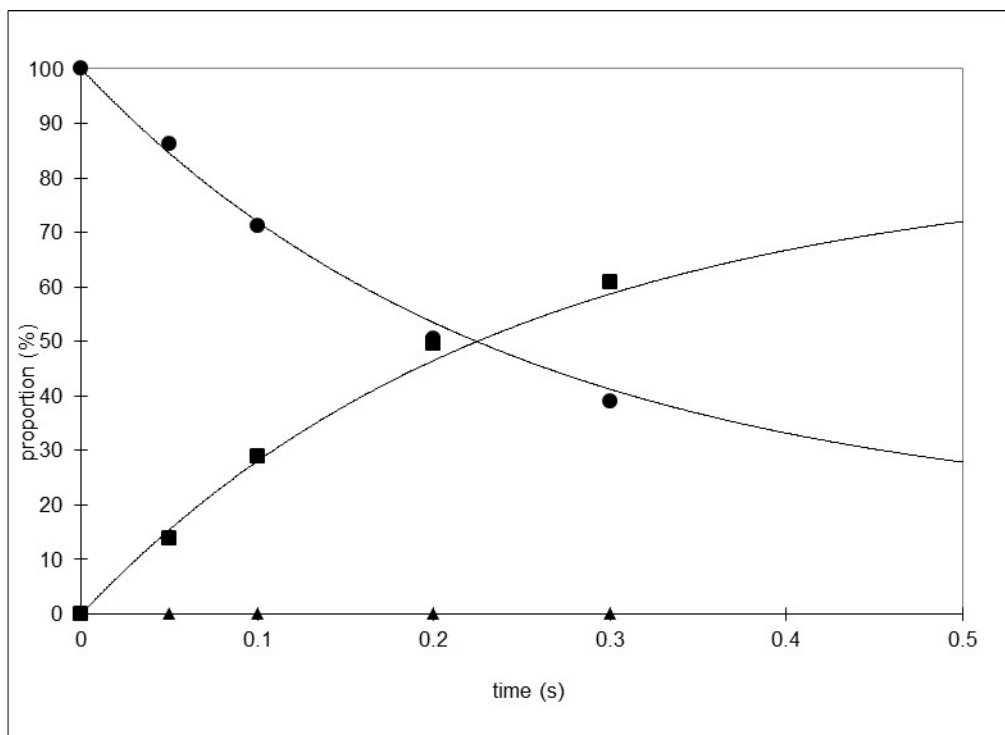
**Fig-S19:** Expansion of the vinyl proton signal region at δ 4.26 showing the signal for 10 under the specified conditions: a): <sup>1</sup>H{<sup>31</sup>P}; b): <sup>1</sup>H; c): <sup>1</sup>H, using Ph<sup>13</sup>CCPh. All spectra recorded at 323 K in methanol-*d*<sub>4</sub>

### 3.0 EXSY data collected from magnetization transfer studies on the reaction intermediates detected in this work



**Fig-S20: Experimental data and simulated kinetic trace for the transfer of the acyl group of **8** into the triflate ester, **2** and *cis* stilbene.**

When the signal at  $\delta$  7.89 for the acyl complex **8** (○) was selectively excited, magnetisation transfer into the  $\delta$  7.69 signal of the triflate ester (●), alongside weaker transfer into the  $\delta$  4.99 of **2** (▲) and the signal for *trans*-stilbene. The relative rates for these conversions are  $0.73\text{ s}^{-1}$ ,  $0.03\text{ s}^{-1}$  and  $0.006\text{ s}^{-1}$  respectively. Analysis of these data requires that the triflate ester reacts to reform **8** with a rate constant of  $3.4\text{ s}^{-1}$ .



**Fig-S21: Experimental data and simulated kinetic trace for the transfer of the triflate ester (●) into the signal for **8** and *cis* stilbene.**

When the signal at  $\delta$  7.69 for the triflate ester (●) is probed in a similar way, rapid transfer into the  $\delta$  7.89 signal of **8** (○) is seen at an identical rate, within error, to that predicted from the observations based on the excitation of **8**.

## 7. References

1. López-Serrano, J., et al., *A para-Hydrogen Investigation of Palladium-Catalyzed Alkyne Hydrogenation*. *Journal of the American Chemical Society*, 2007. **129**(20): p. 6513-6527.
2. Duckett, S.B. and R.E. Mewis, *Application of Parahydrogen Induced Polarization Techniques in NMR Spectroscopy and Imaging*. *Accounts of Chemical Research*, 2012. **45**(8): p. 1247-1257.