

Electronic Supporting Information for:

Bimetallic N-Heterocyclic Carbene Rh(I) Complexes: Probing the Cooperative Effect for the Catalyzed Hydroelementation of Alkynes

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Figure S1: κ^2 -mono (**9**), ^1H NMR (DMSO- d_6 , 300 MHz)

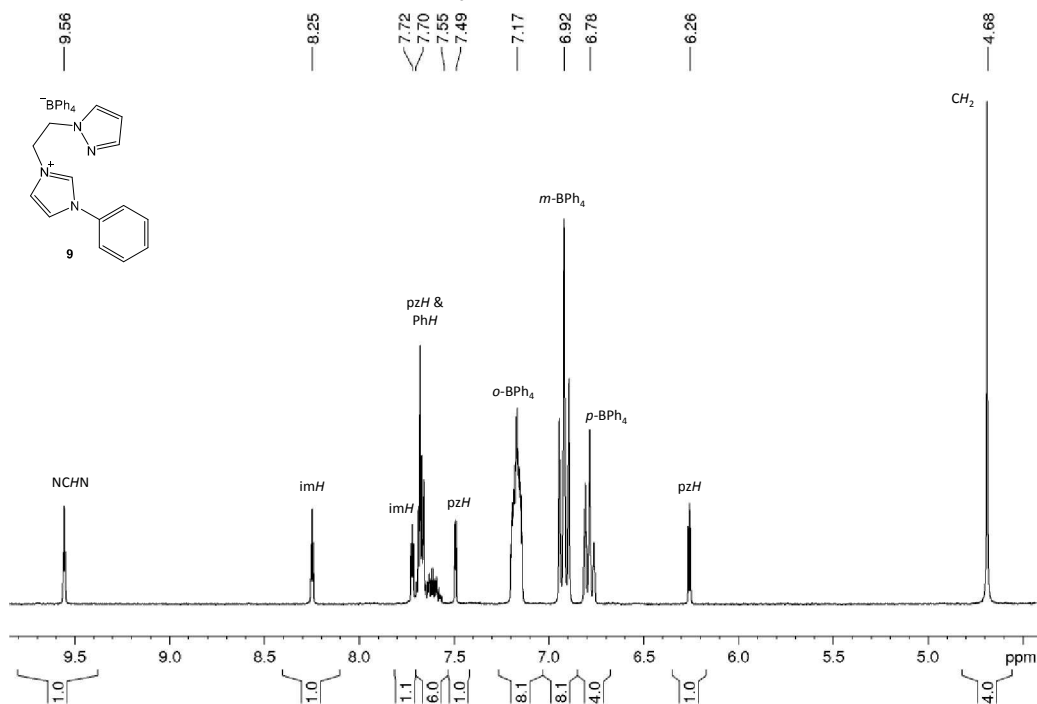


Figure S2: κ^2 -mono (**9**), ^{13}C NMR (DMSO- d_6 , 75 MHz)

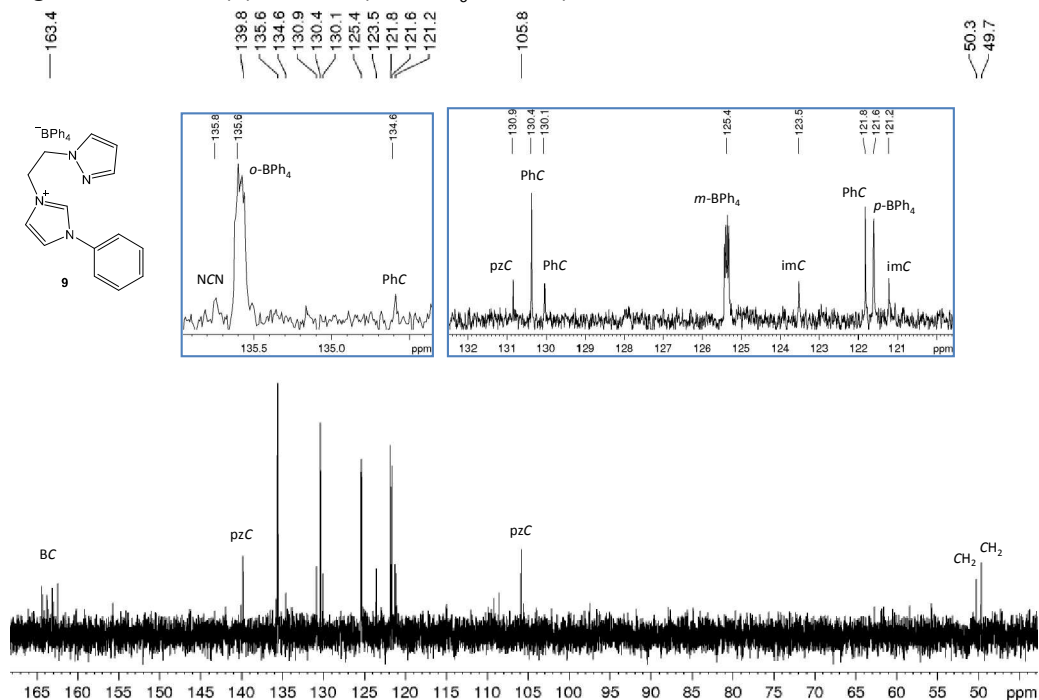


Figure S3: κ^2 -ortho (**10**), ^1H NMR (Acetone- d_6 , 300 MHz)

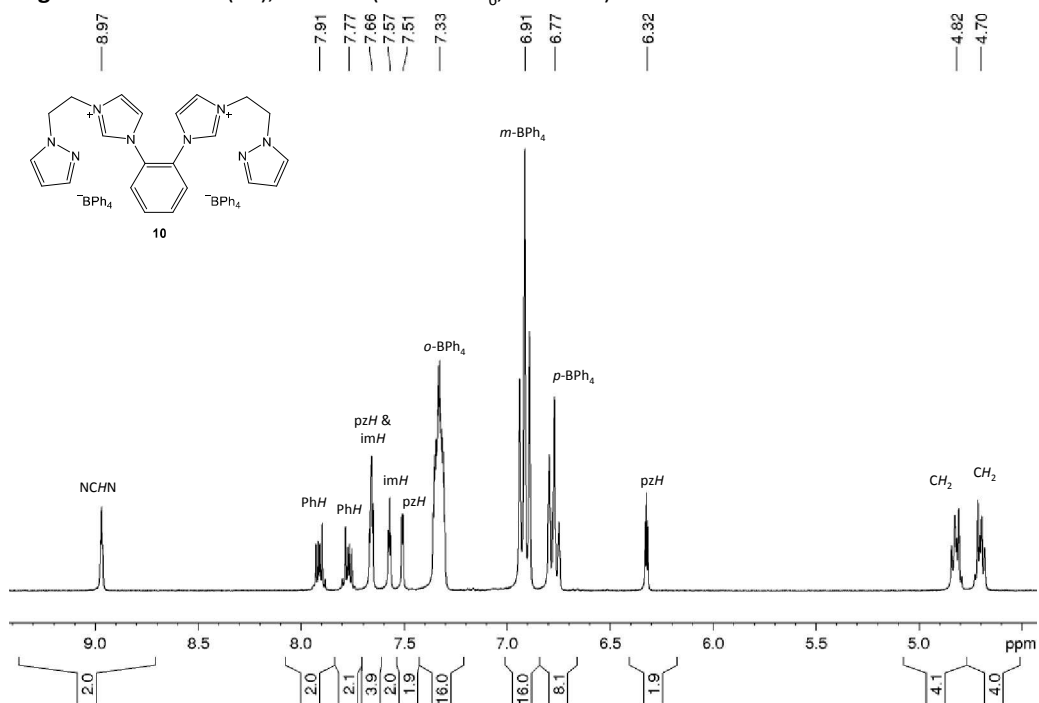


Figure S4: κ^2 -ortho (**10**), ^{13}C NMR (Acetone- d_6 , 75 MHz)

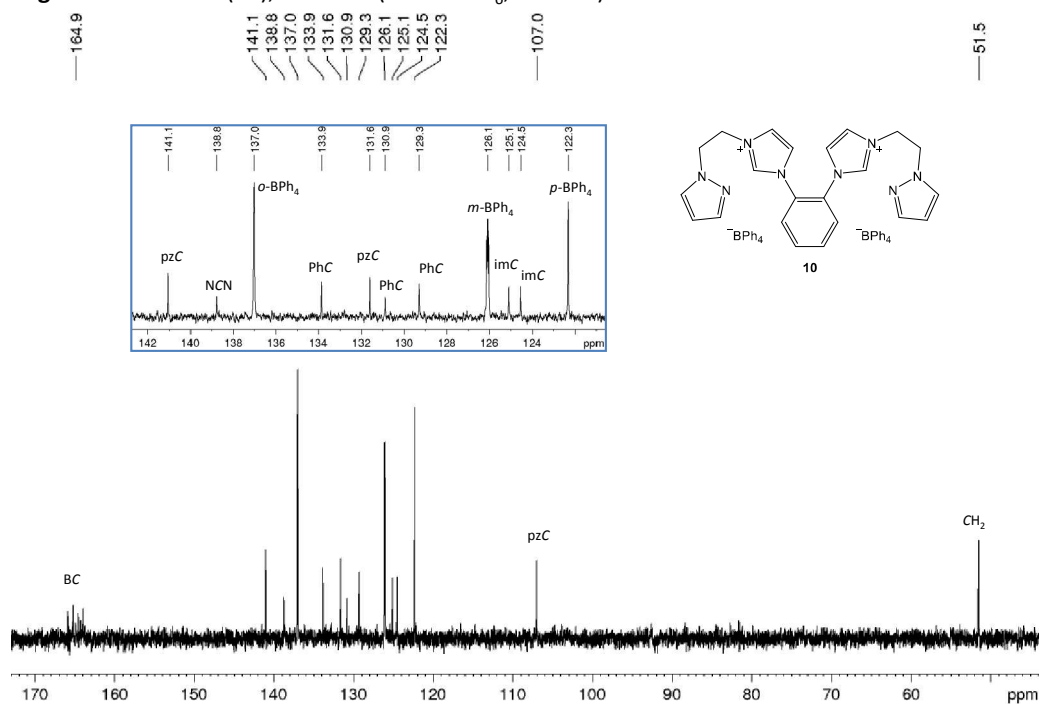


Figure S5: κ^2 -meta (**11**), ^1H NMR (Acetone- d_6 , 500 MHz)

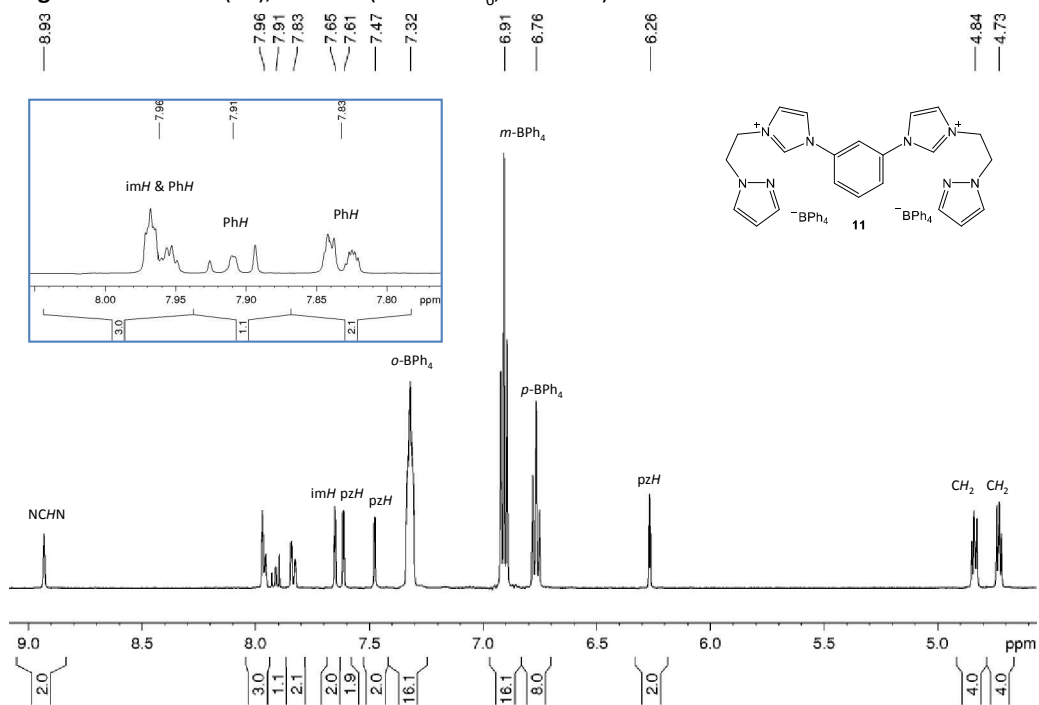


Figure S6: κ^2 -meta (**11**), ^{13}C NMR (Acetone- d_6 , 125 MHz)

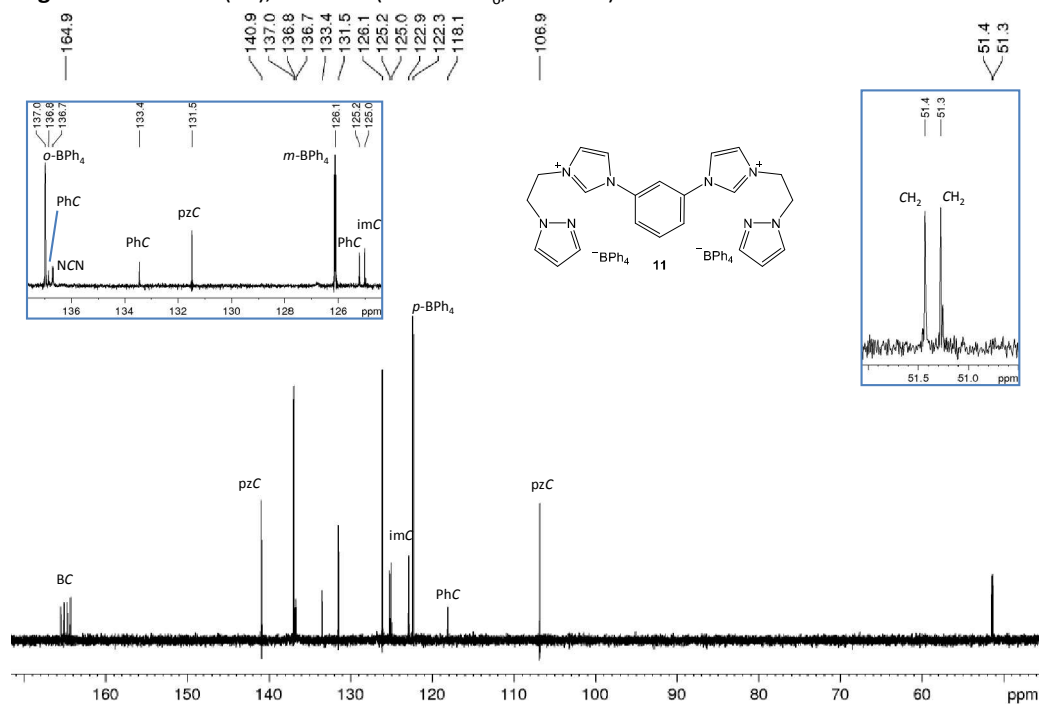


Figure S7: κ^1 -mono-Rh(COD) (**12**), ^1H NMR (CDCl_3 , 400 MHz)

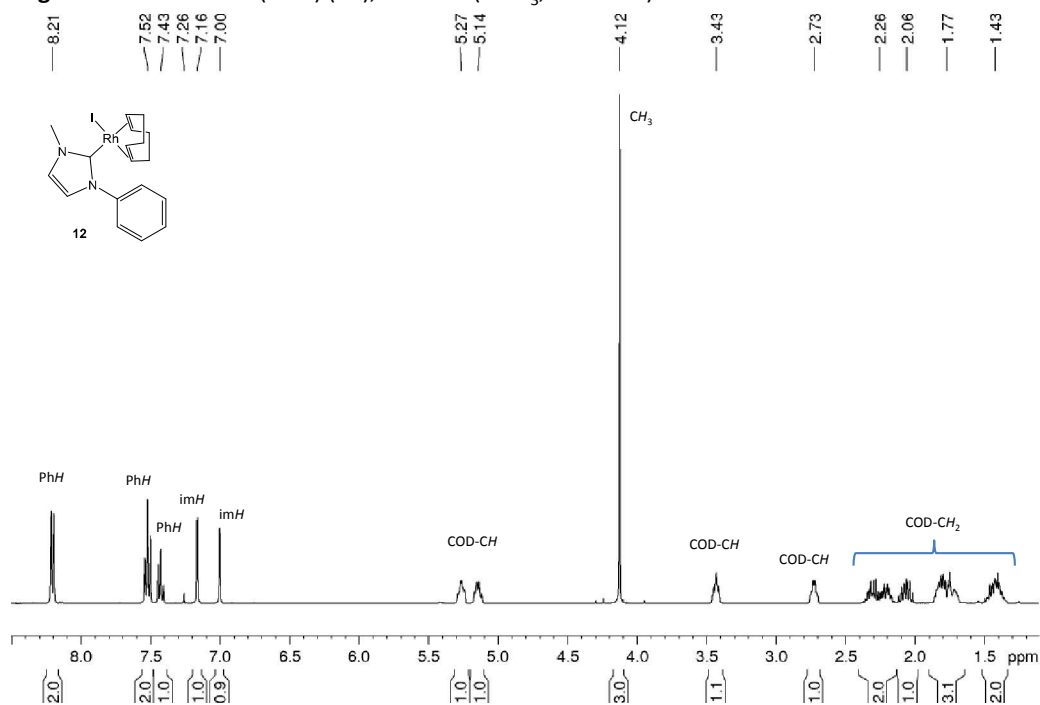


Figure S8: κ^1 -mono-Rh(COD) (**12**), ^{13}C NMR (CDCl_3 , 100 MHz)

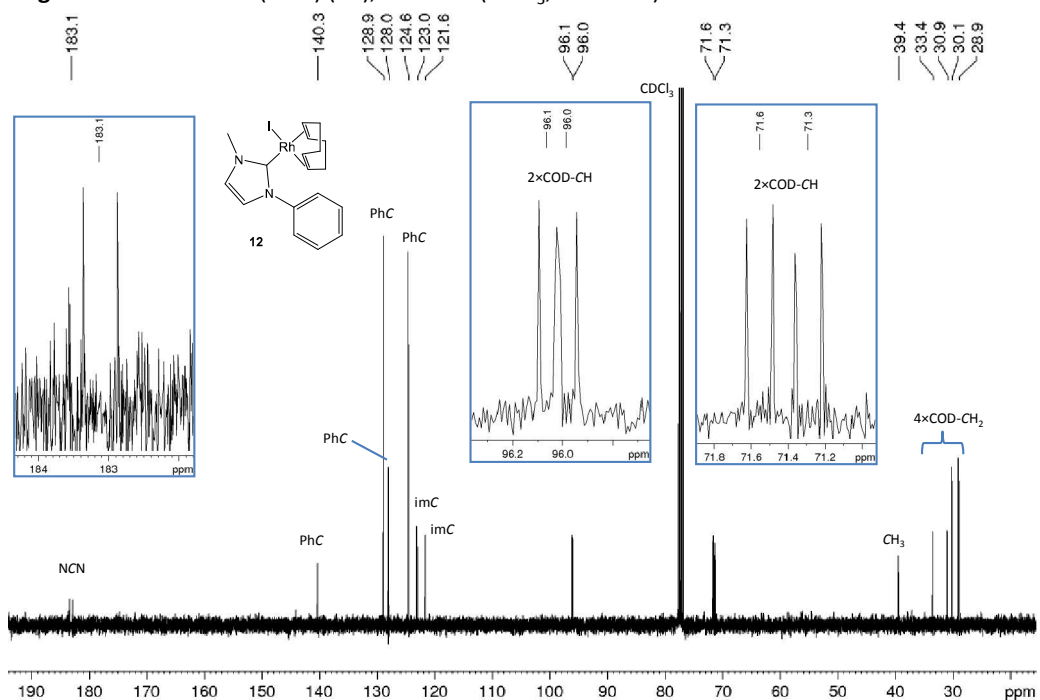


Figure S9: κ^1 -*meta*-Rh(COD) (**13**), ^1H NMR (CDCl_3 , 300 MHz)

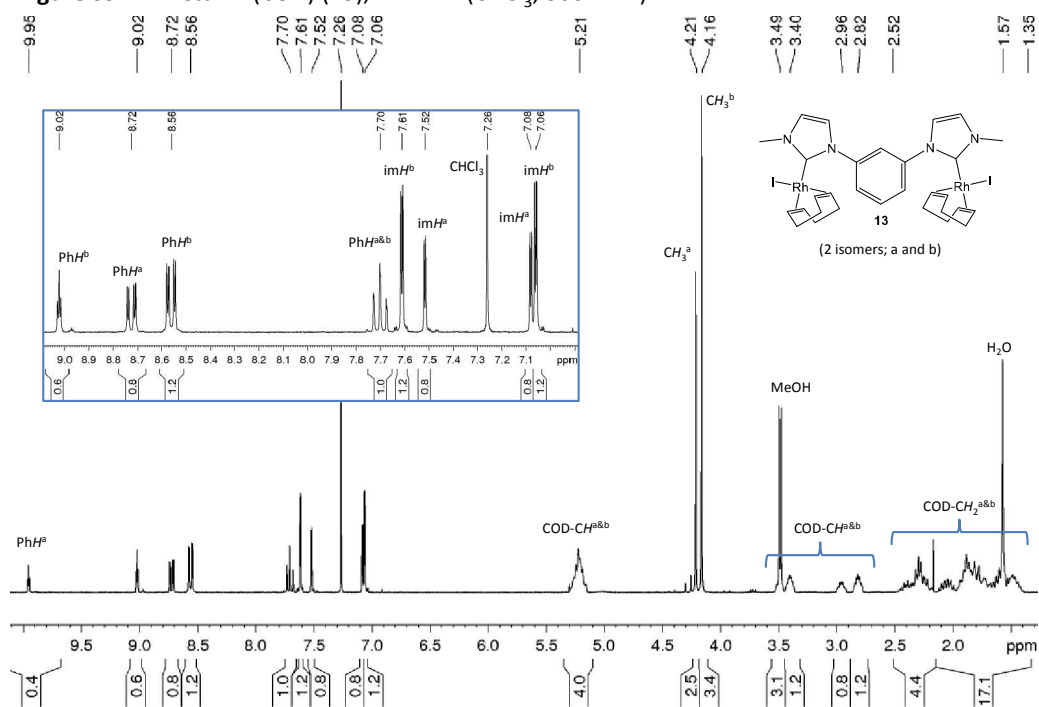


Figure S10: κ^1 -*meta*-Rh(COD) (**13**), ^{13}C NMR (CDCl_3 , 75 MHz)

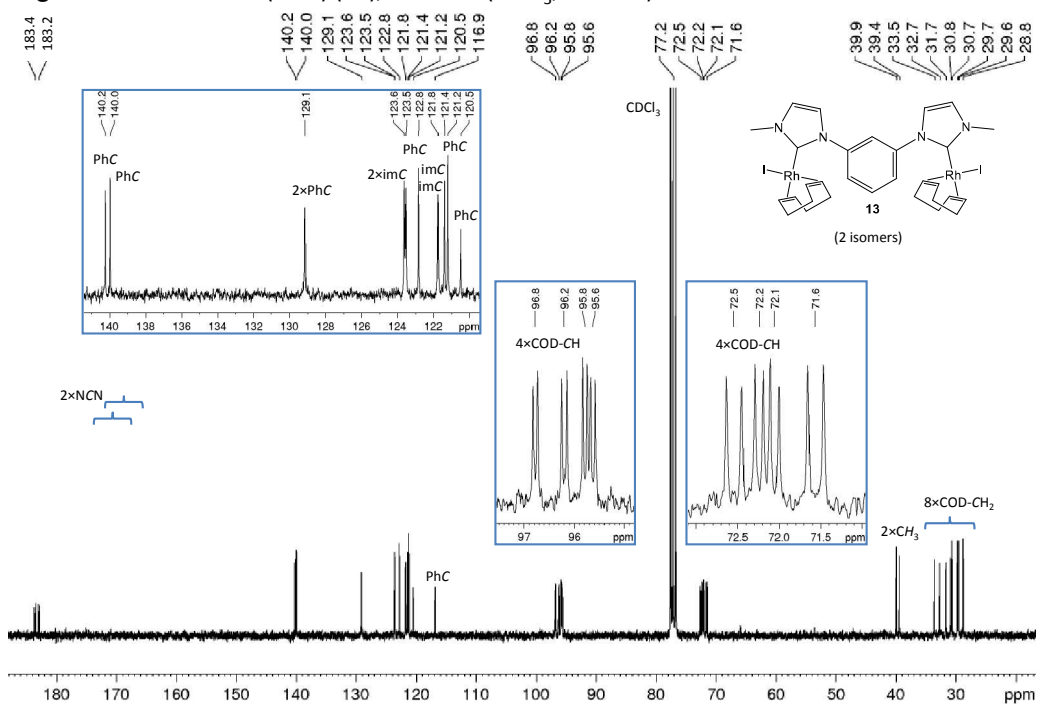


Figure S11: κ^1 -*para*-Rh(COD) (**14**), ^1H NMR (CDCl_3 , 300 MHz)

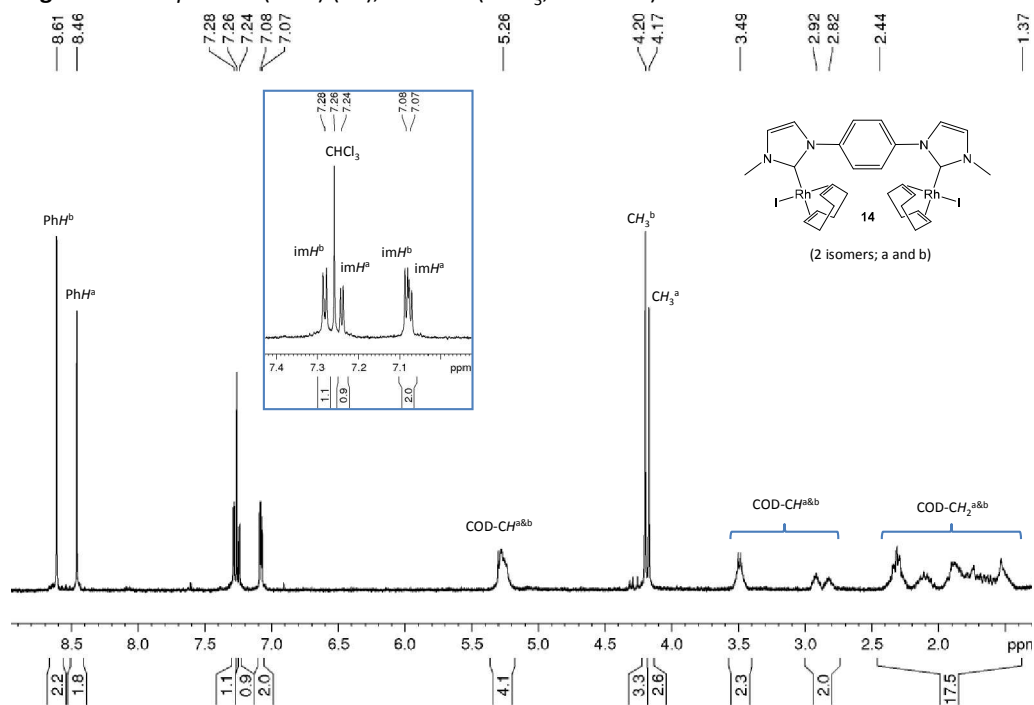
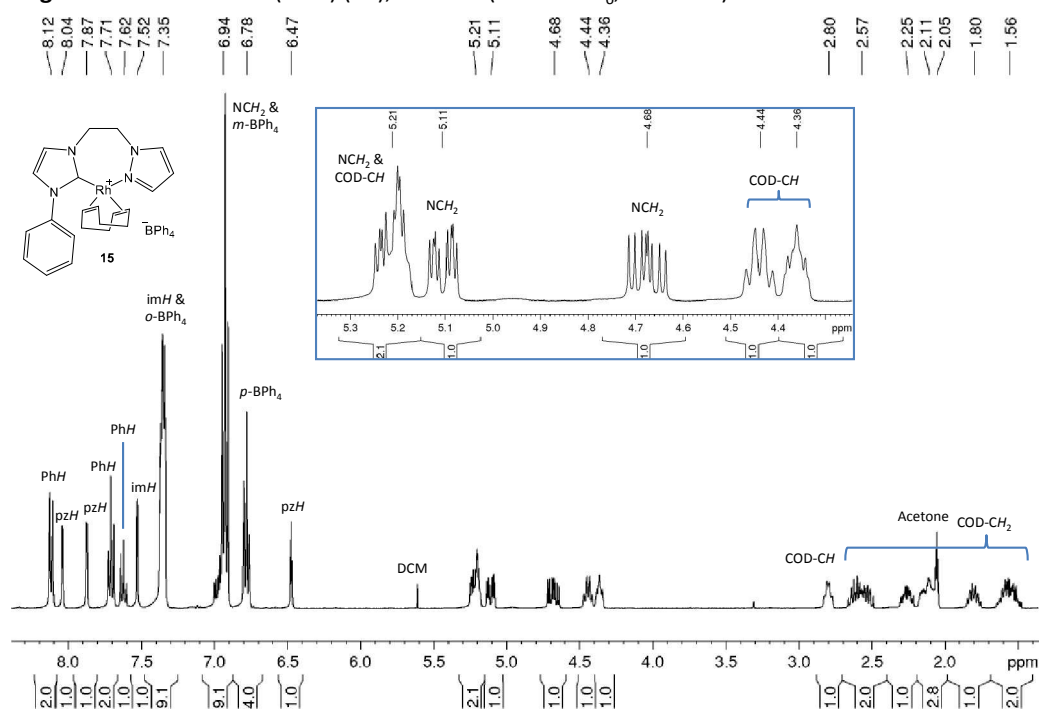


Figure S12: κ^2 -*mono*-Rh(COD) (**15**), ^1H NMR ($\text{Acetone-}d_6$, 400 MHz)



176.4 — 165.0 — 141.9 141.5 137.1 134.9 130.3 129.8 126.0 125.6 125.3 123.8 122.3 — 109.2 — 97.2 — 95.1 — 80.3 — 74.7 — 51.4 50.3 — 34.6 30.8 28.4

PhC *m*-BPh₄ PhC *p*-BPh₄ COD-CH COD-CH COD-CH COD-CH

PhC imC imC

o-BPh₄

BC NCN pzC PhC pzC pzC NCH₂ NCH₂

Acetone-CD₃

30.3 (HSQC)

COD-CH₂

ppm

Chemical structure of compound 16 is shown on the left. The structure consists of two 1,5-diphenyl-1,5-dihydro-2H-pyrazole units linked by a central diphenylmethyl group. The structure is labeled (2 isomers; a and b).

The ^1H NMR spectrum (CDCl₃) shows the following peaks and assignments:

- Aromatic region (6.5–8.3 ppm):** Peaks are assigned to PhH^b , PhH^a , $m\text{-BPh}_4$, $o\text{-BPh}_4$, and $p\text{-BPh}_4$. The inset shows a detailed view of this region with assignments for PhH^b , pzh^b , imH^b , imH^a , pzh^a , and PhH^a .
- Aliphatic region (1.5–3.5 ppm):** Peaks are assigned to $\text{NCH}_2^{a\&b}$ & $\text{COD-CH}^{a\&b}$, $\text{COD-CH}^{a\&b}$, and $\text{COD-CH}_2^{a\&b}$.

Integration values are provided below the baseline:

- PhH^b : 2.0
- PhH^a : 4.0
- $m\text{-BPh}_4$: 2.0
- $o\text{-BPh}_4$: 2.2
- $p\text{-BPh}_4$: 17.4
- $\text{NCH}_2^{a\&b}$ & $\text{COD-CH}^{a\&b}$: 29.5
- $\text{COD-CH}^{a\&b}$: 2.1
- $\text{COD-CH}_2^{a\&b}$: 12.2
- $\text{COD-CH}^{a\&b}$: 14.3
- $\text{COD-CH}_2^{a\&b}$: 6.1

Figure S15: κ^2 -*meta*-Rh(COD) (**16**), ^{13}C NMR (Acetone- d_6 , 100 MHz)

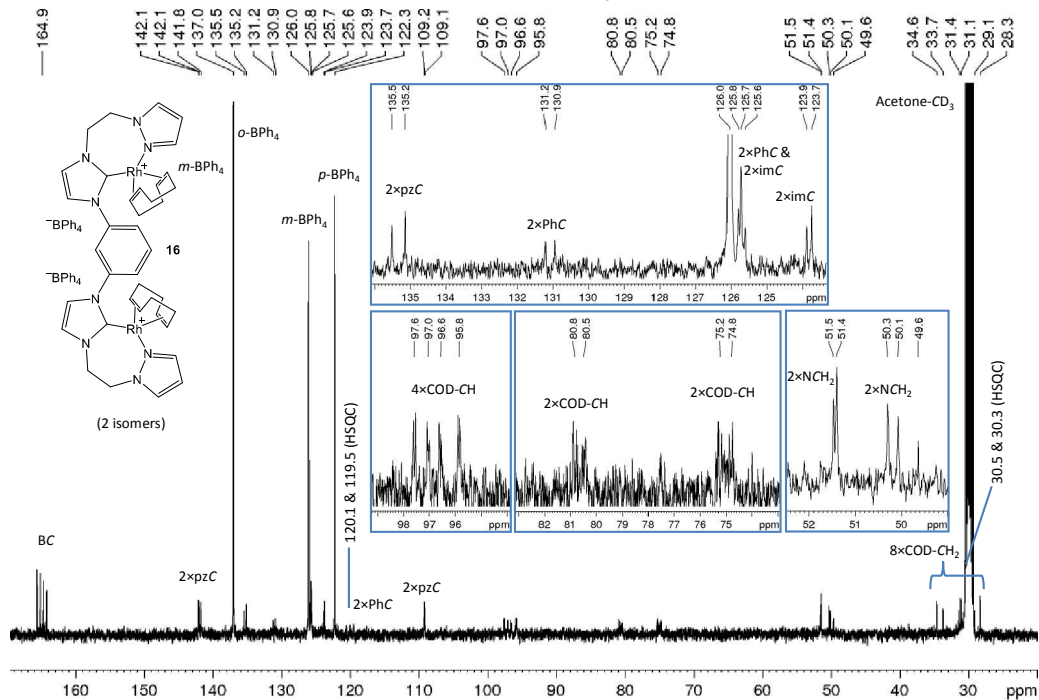


Figure S16: κ^1 -*mono*-Rh(CO)₂ (**17**), ^1H NMR (CDCl₃, 600 MHz)

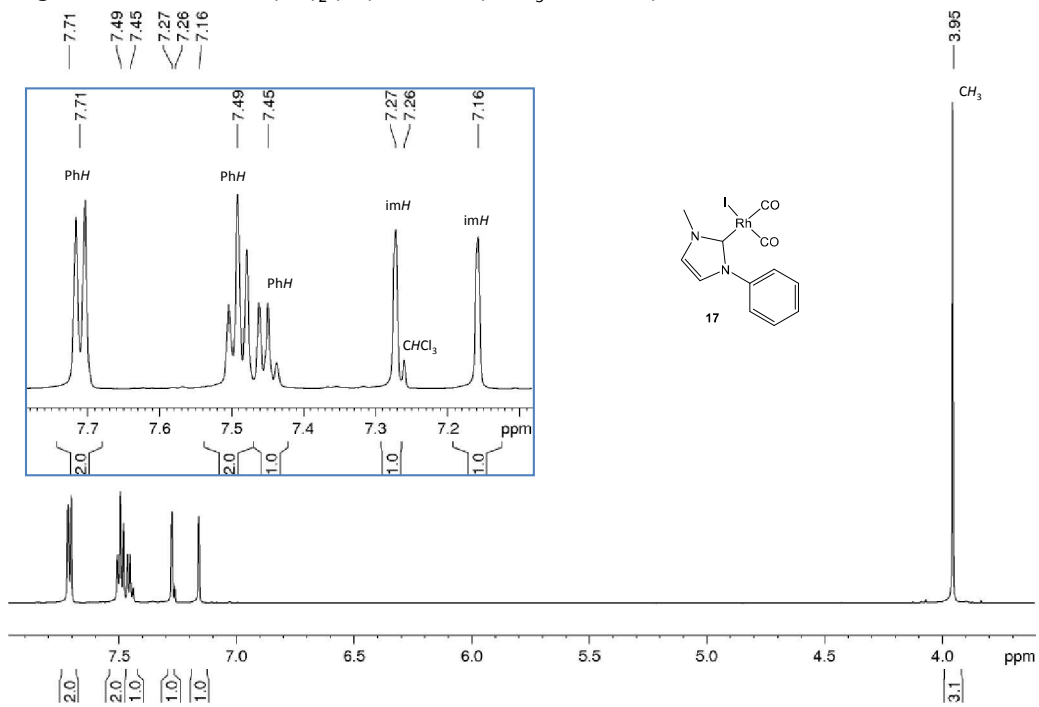


Figure S17: κ^1 -mono-Rh(CO)₂ (**17**), ¹³C NMR (CDCl₃, 150 MHz)

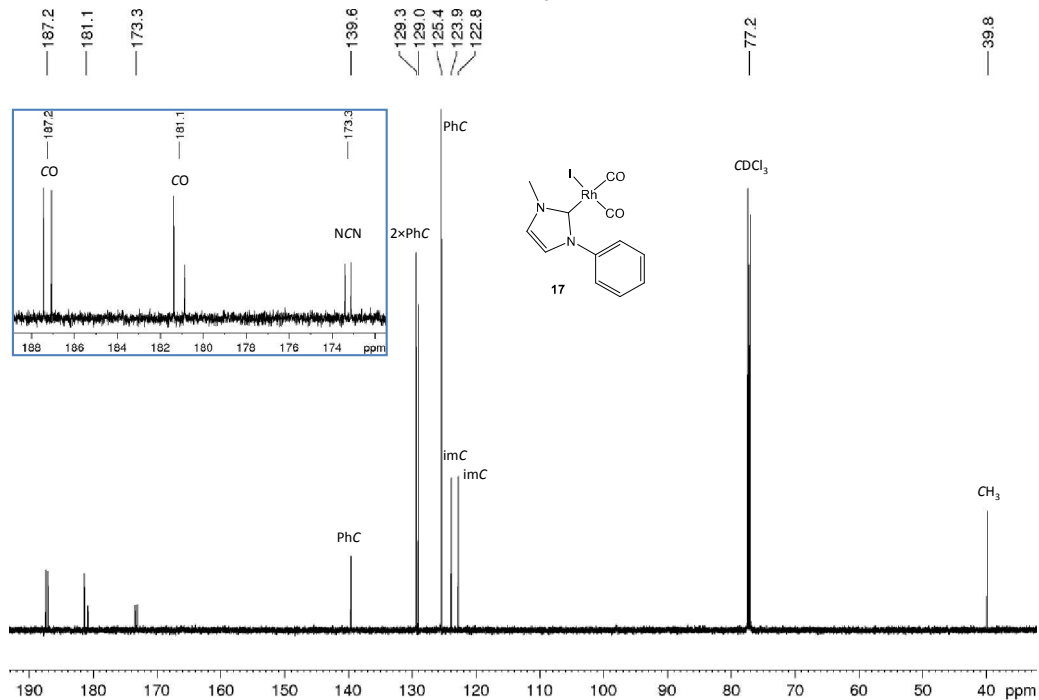


Figure S18: κ^1 -meta-Rh(CO)₂ (**18**), ¹H NMR (CDCl₃, 400 MHz, 250 K)

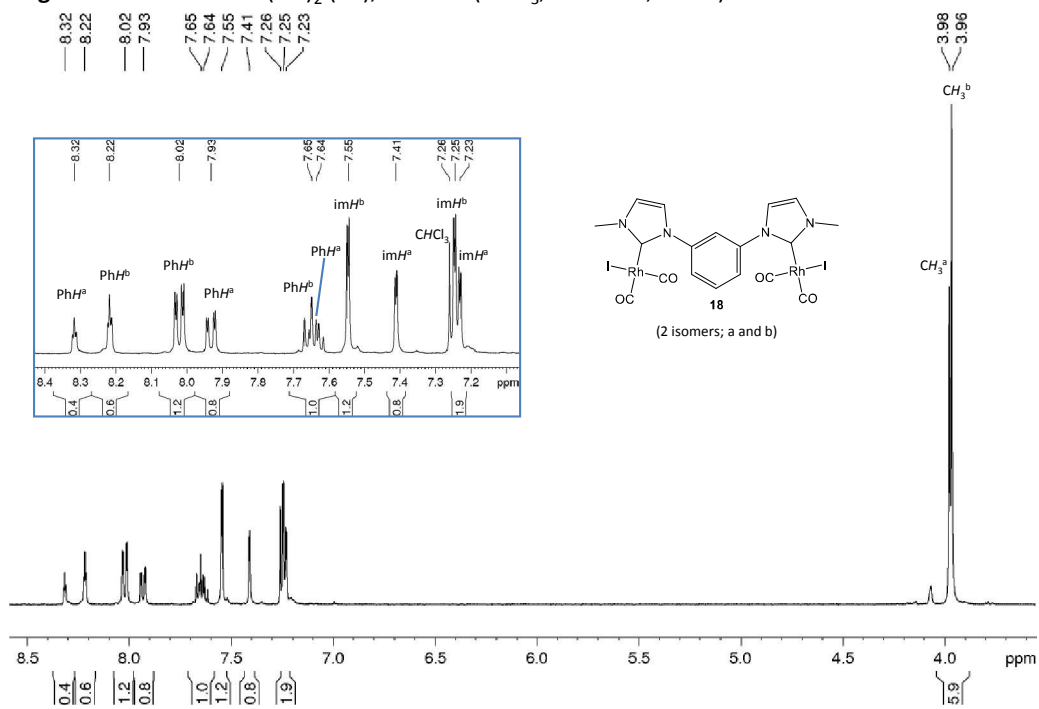


Figure S19: κ^1 -*meta*-Rh(CO)₂ (**18**), ¹³C NMR (CDCl₃, 100 MHz, 250 K)

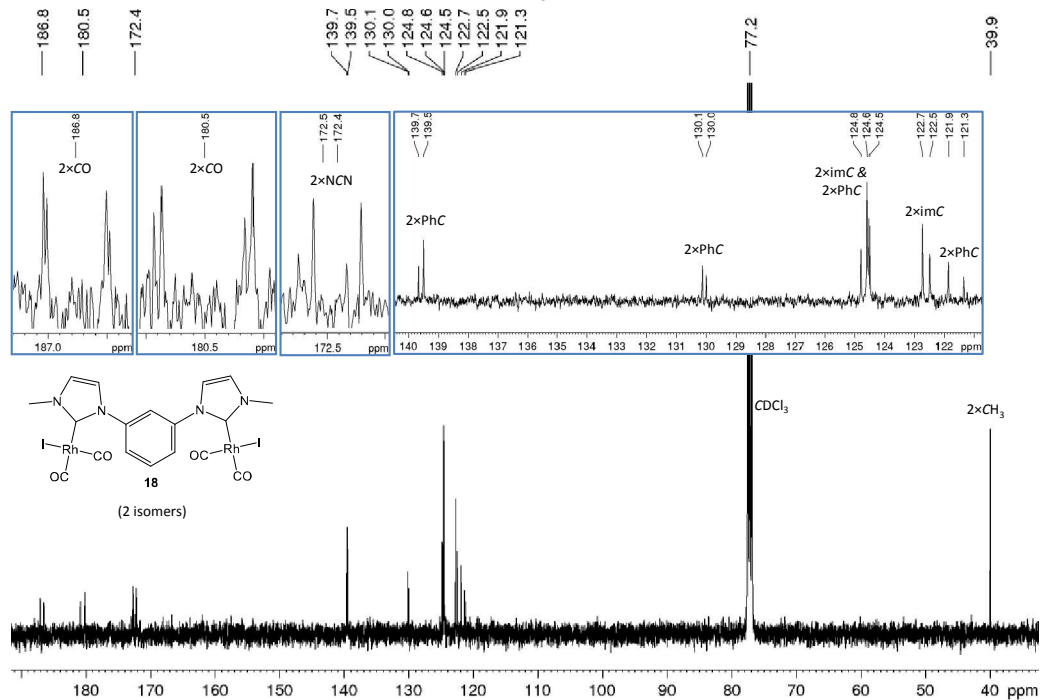


Figure S20: κ^1 -*meta*-Rh(CO)₂ (**18**), ¹H NMR (CDCl₃); (a) 300 MHz, 298 K, (b) 400 MHz, 250 K.

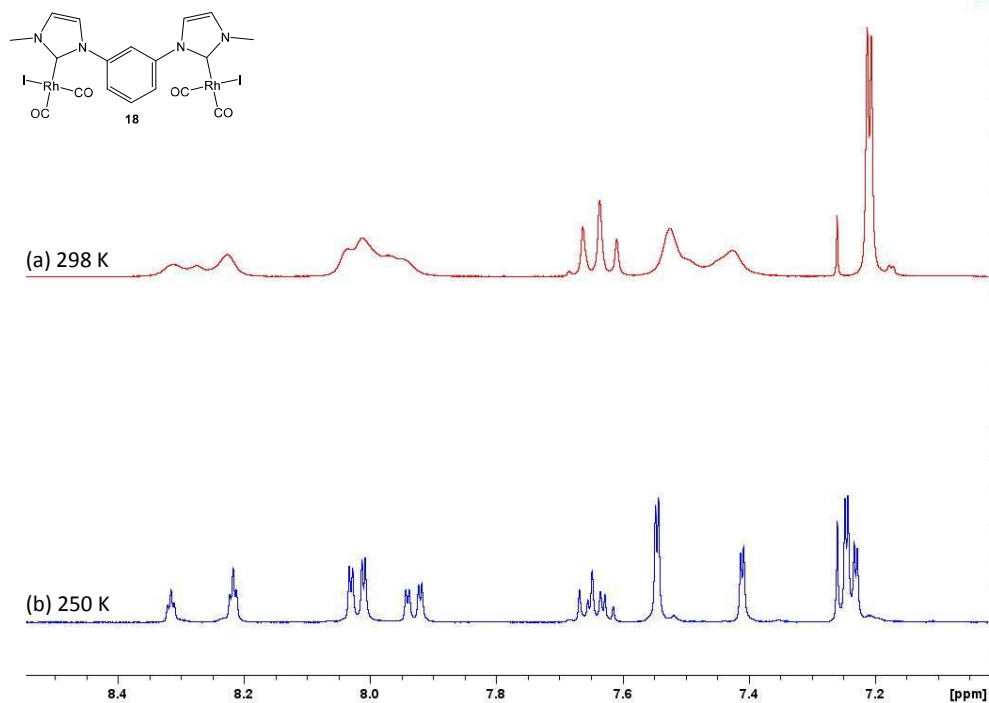


Figure S21: κ^1 -*para*-Rh(CO)₂ (**19**), ¹H NMR (CDCl₃, 300 MHz)

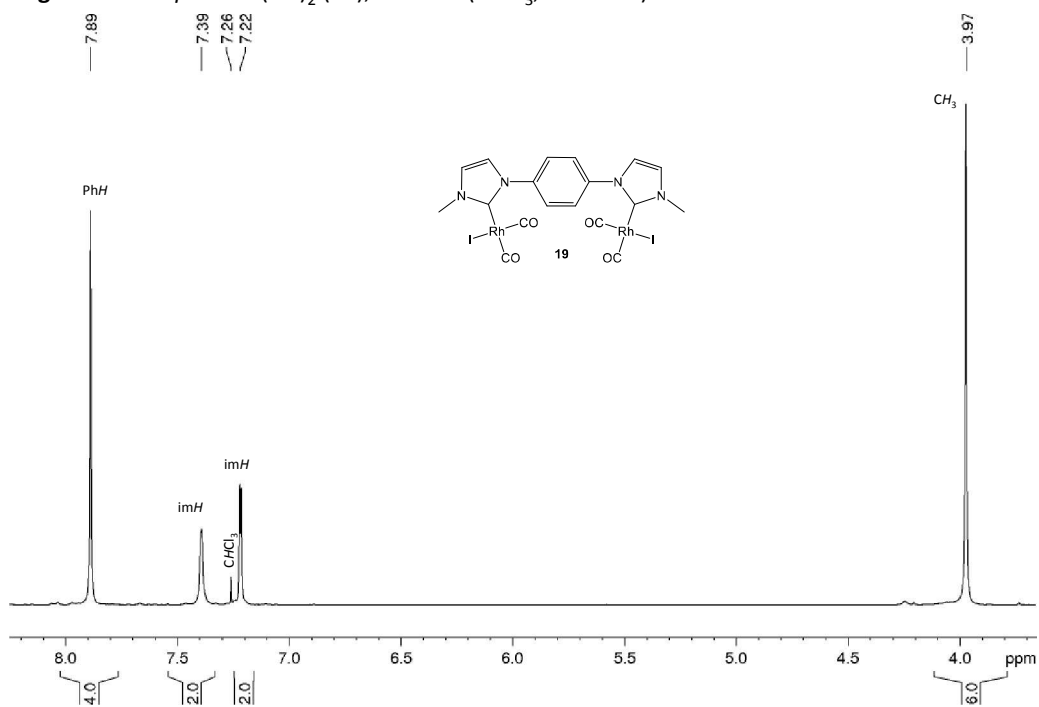


Figure S22: κ^1 -*para*-Rh(CO)₂ (**19**), ¹³C NMR (CDCl₃, 75 MHz)

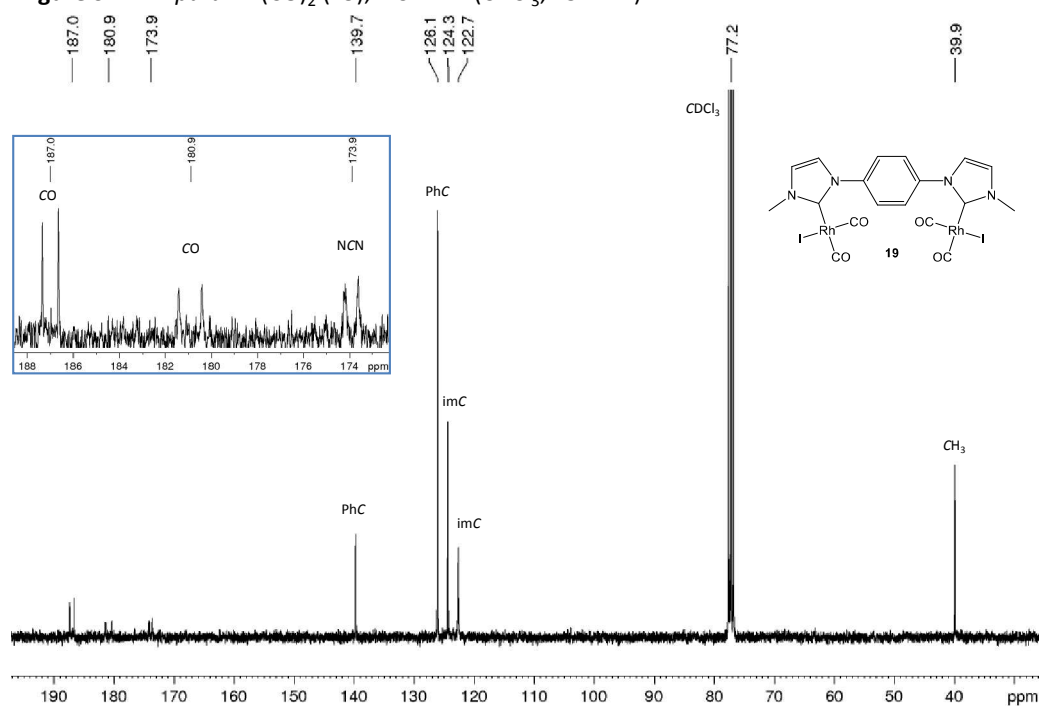


Figure S23: κ^2 -mono-Rh(CO)₂ (**20**), ¹H NMR (Acetone-*d*₆, 400 MHz)

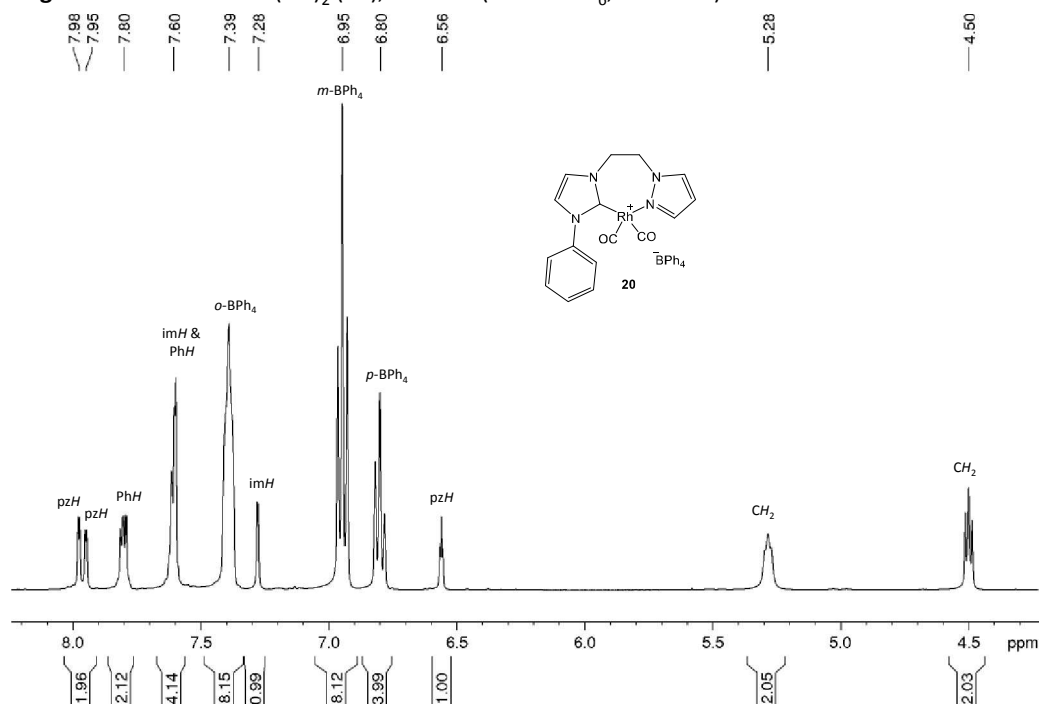


Figure S24: κ^2 -mono-Rh(CO)₂ (**20**), ¹³C NMR (Acetone-*d*₆, 100 MHz)

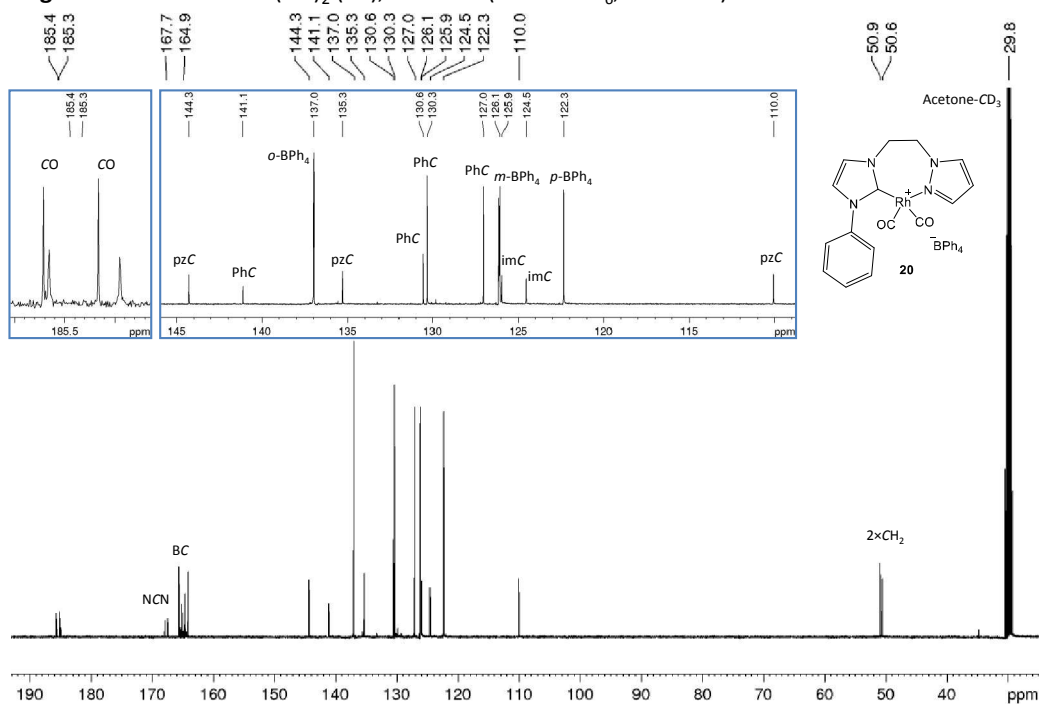


Figure S25: κ^2 -meta-Rh(CO)₂ (**21**), ¹H NMR (Acetone-*d*₆, 400 MHz)

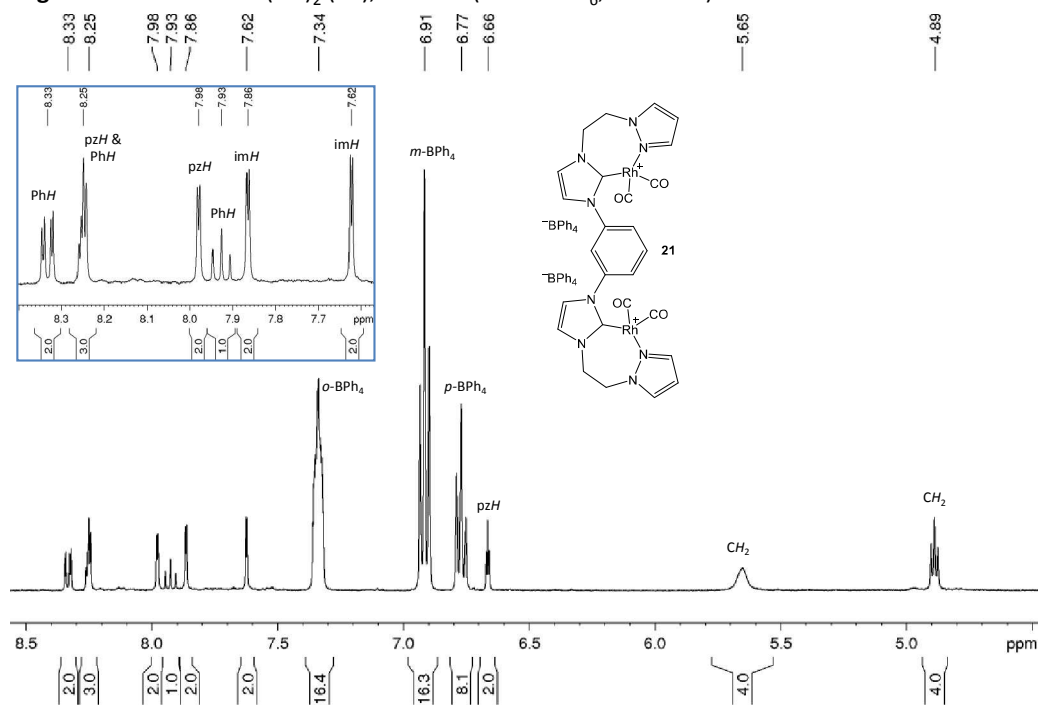


Figure S26: κ^2 -meta-Rh(CO)₂ (**21**), ¹³C NMR (Acetone-*d*₆, 100 MHz)

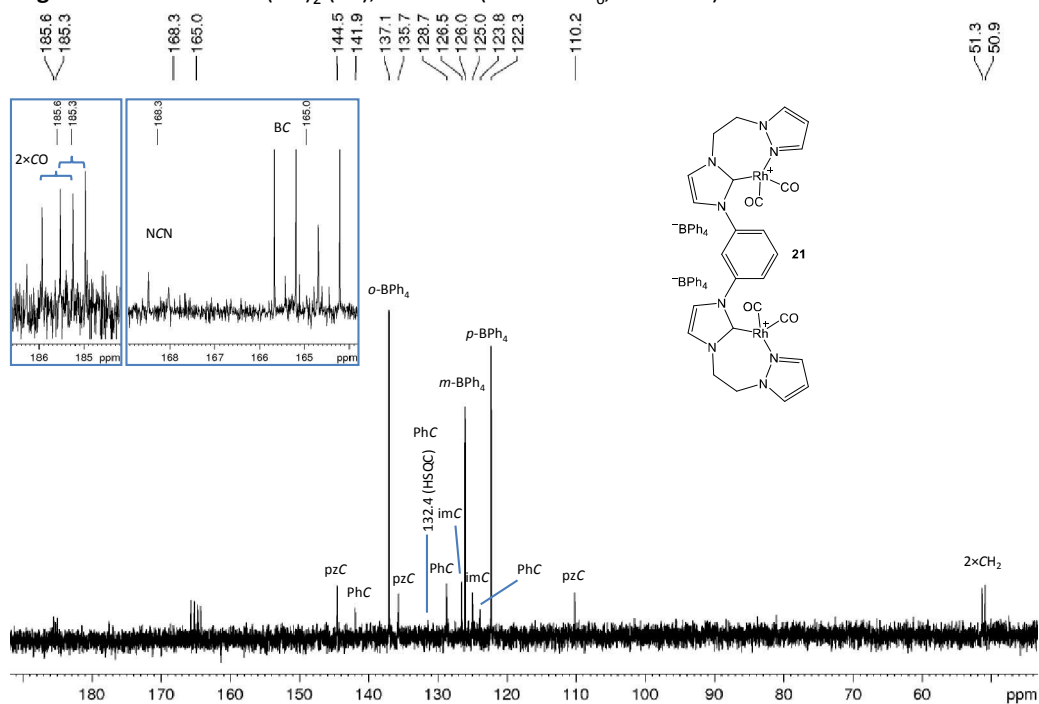


Figure S27: Dihydroalkoxylation reaction mixture, ^1H NMR ($\text{TCE-}d_2$, 500 MHz)

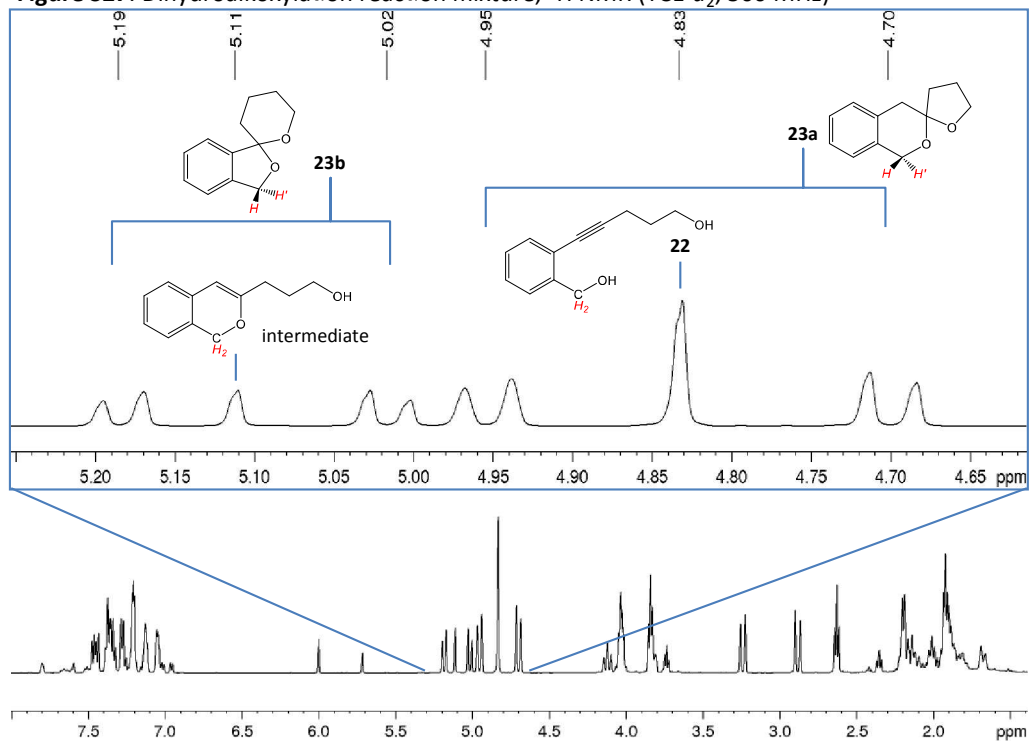


Figure S28: Hydrosilylation reaction mixture, ^1H NMR ($\text{THF-}d_8$, 500 MHz)

