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**: κ²-*mono* (**9**), $^{1}$H NMR (DMSO-$d_6$, 300 MHz)

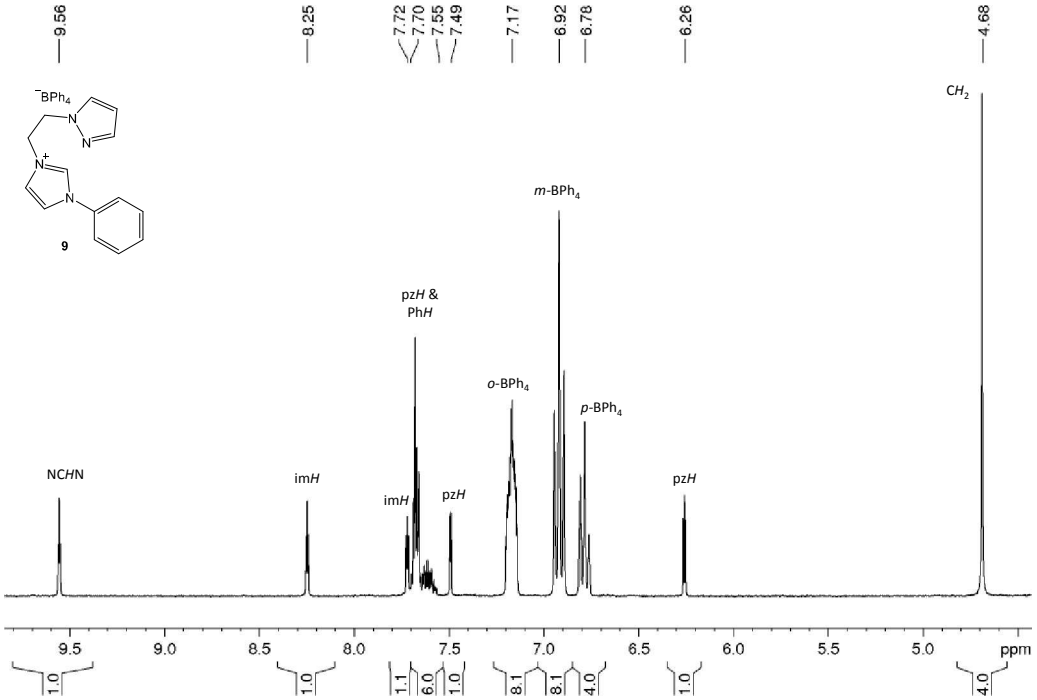


**Figure S2**: κ²-*mono* (**9**), $^{13}$C NMR (DMSO-$d_6$, 75 MHz)

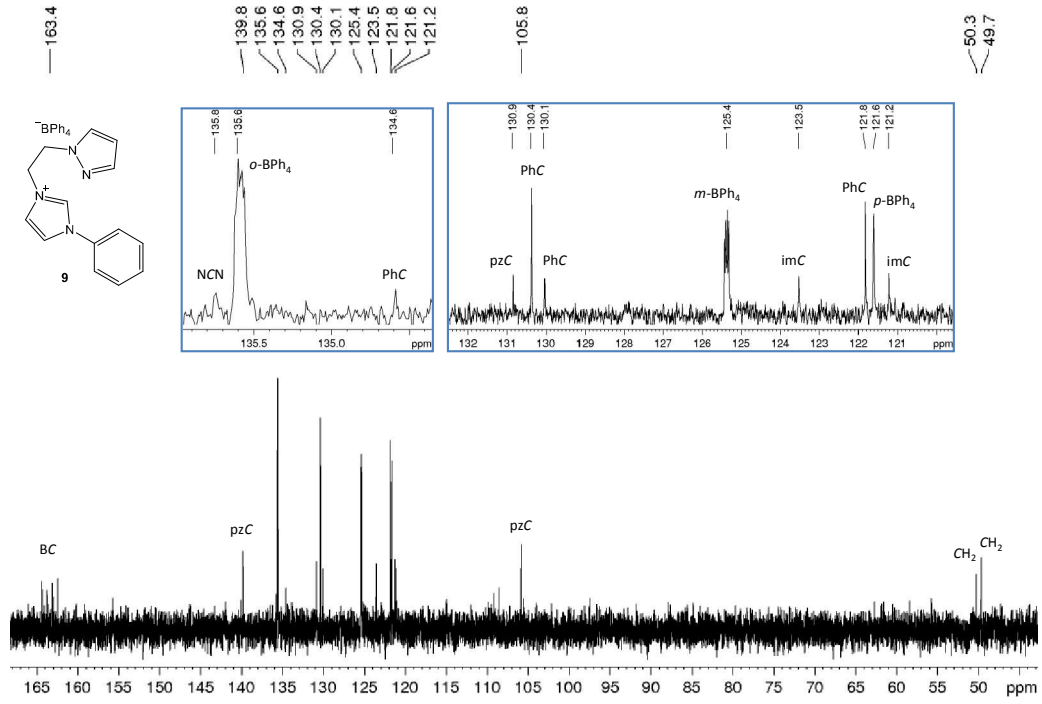

**Figure S3**: κ²-*ortho* (**10**), $^{1}$H NMR (Acetone-$d_6$, 300 MHz)

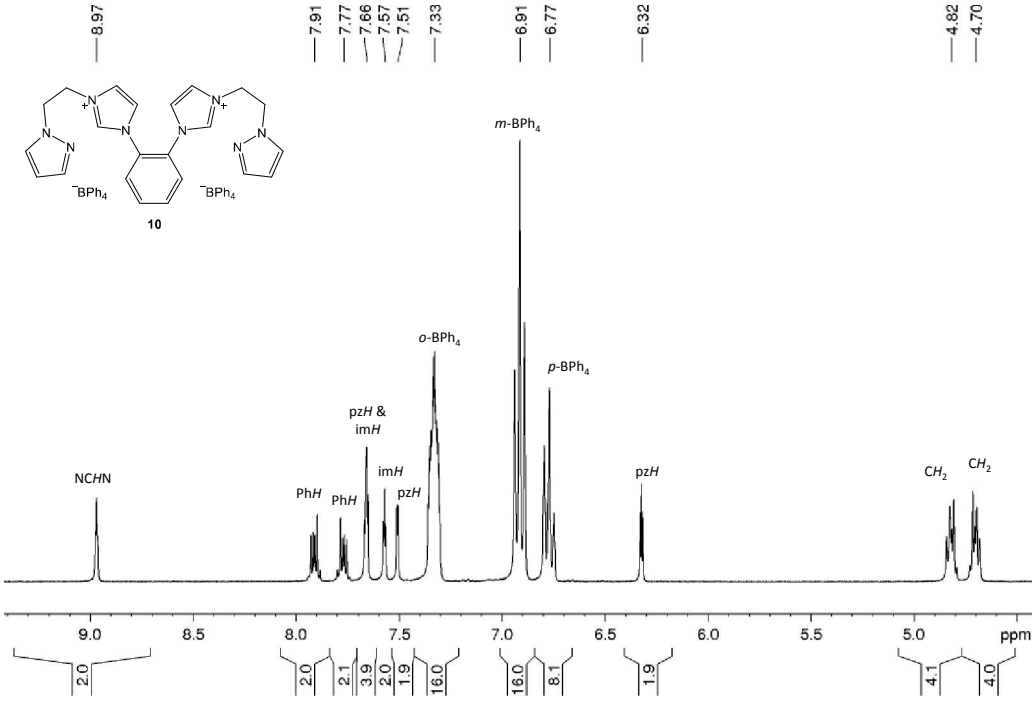


**Figure S4**: κ²-*ortho* (**10**), $^{13}$C NMR (Acetone-$d_6$, 75 MHz)

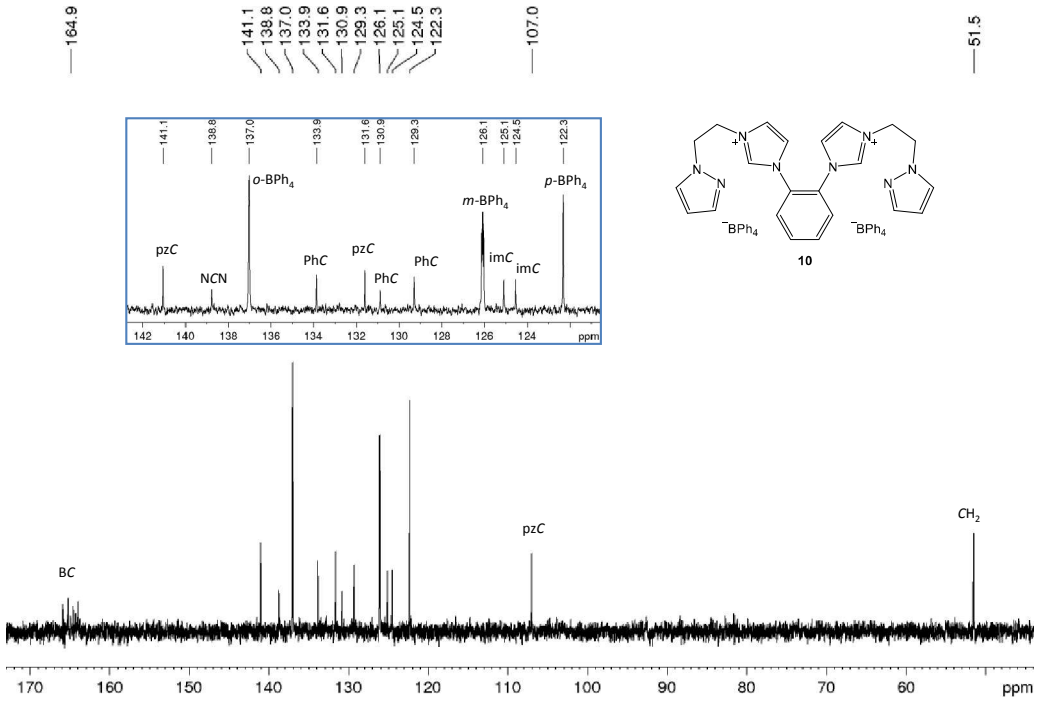

**Figure S5**: κ²-*meta* (**11**), $^{1}$H NMR (Acetone-$d_6$, 500 MHz)

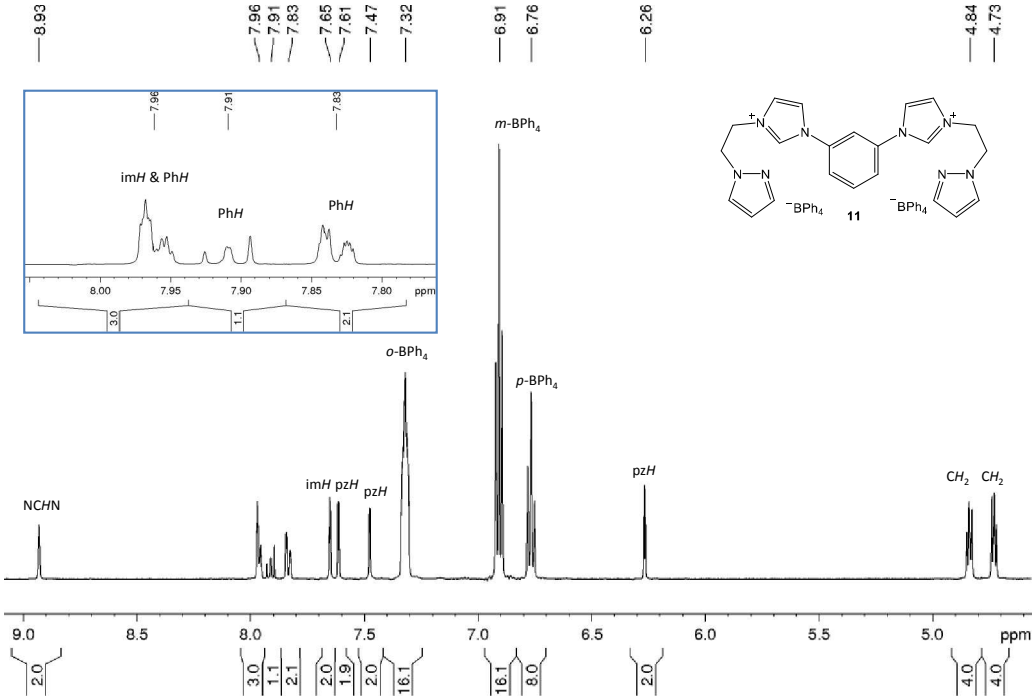


**Figure S6**: κ²-*meta* (**11**), $^{13}$C NMR (Acetone-$d_6$, 125 MHz)

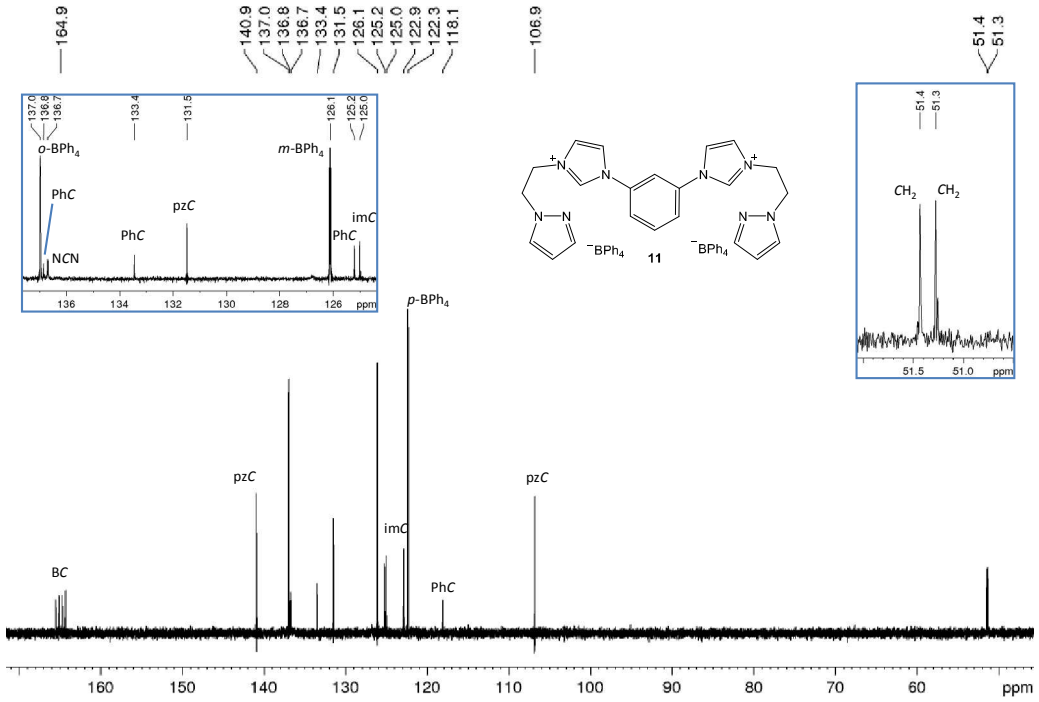

**Figure S7**: κ$^1$-*mono*-Rh(COD) (**12**), $^1$H NMR ($CDCl_3$, 400 MHz)

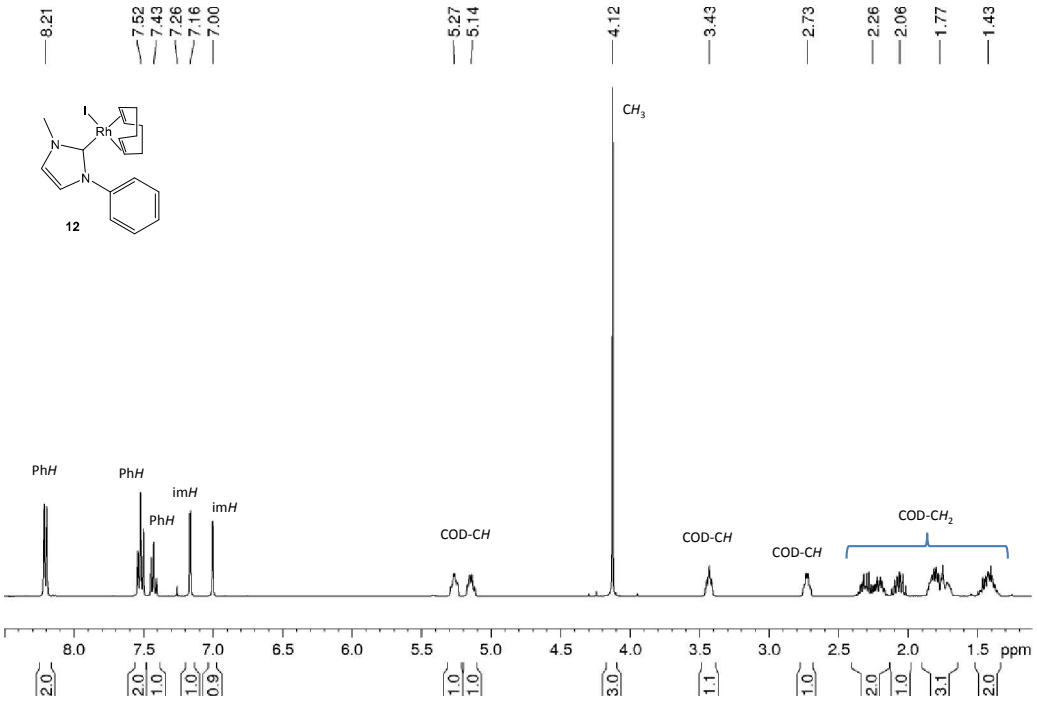


**Figure S8**: κ$^1$-*mono*-Rh(COD) (**12**), $^{13}$C NMR ($CDCl_3$, 100 MHz)

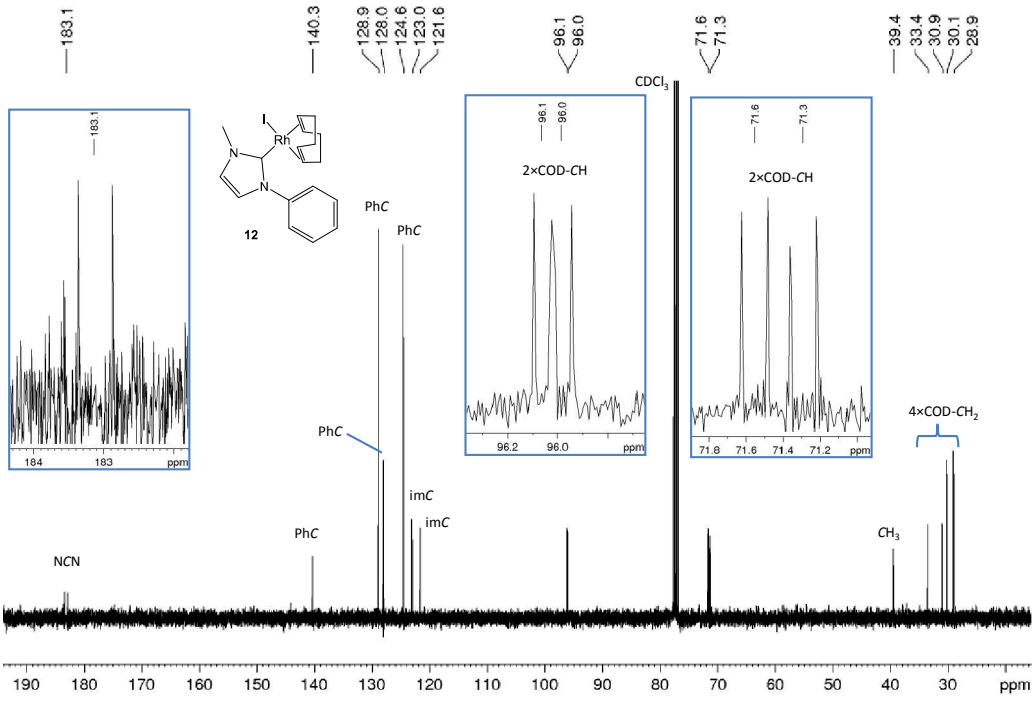

**Figure S9**: $\kappa^1$-*meta*-Rh(COD) (**13**), $^1$H NMR ($CDCl_3$, 300 MHz)

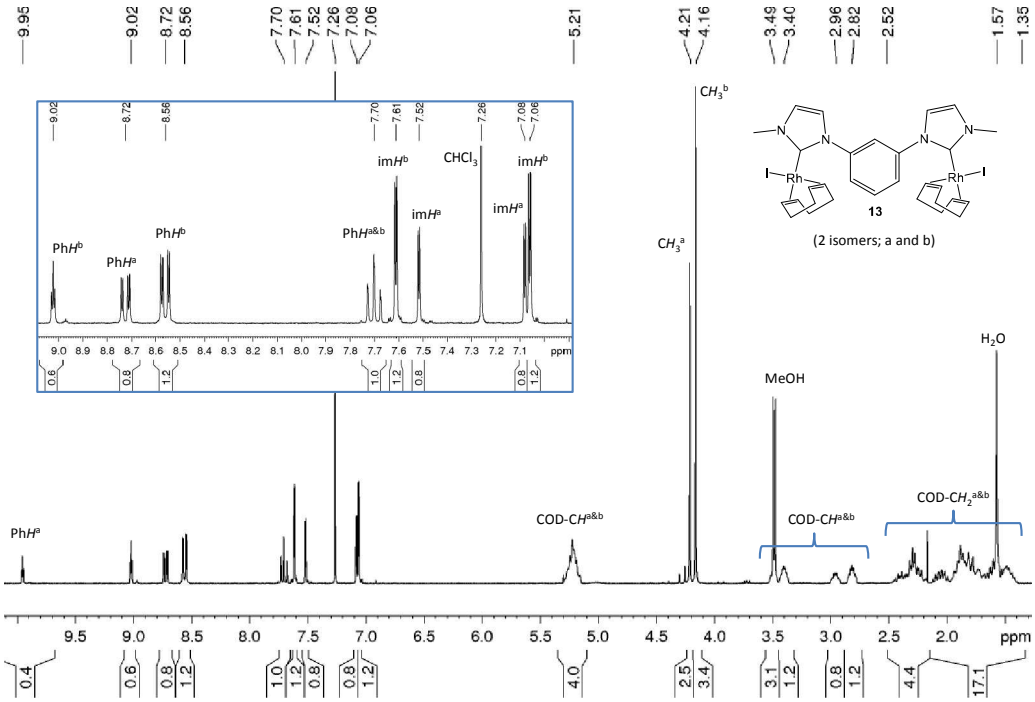


**Figure S10**: $\kappa^1$-*meta*-Rh(COD) (**13**), $^{13}$C NMR ($CDCl_3$, 75 MHz)

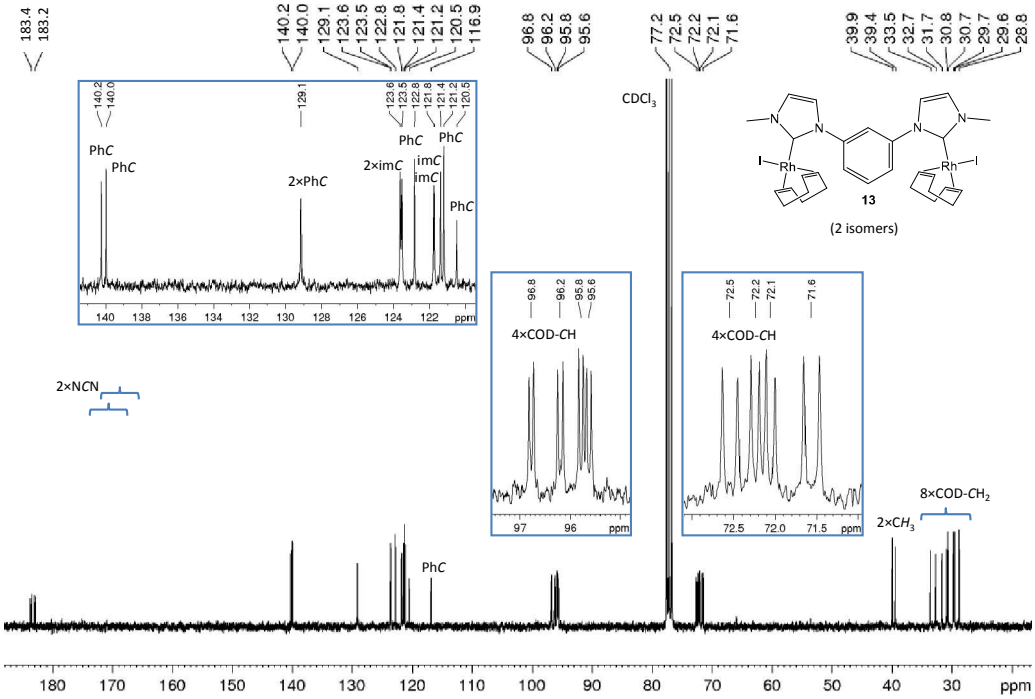

**Figure S11**: κ[1]-*para*-Rh(COD) (**14**), $^1$H NMR ($CDCl_3$, 300 MHz)

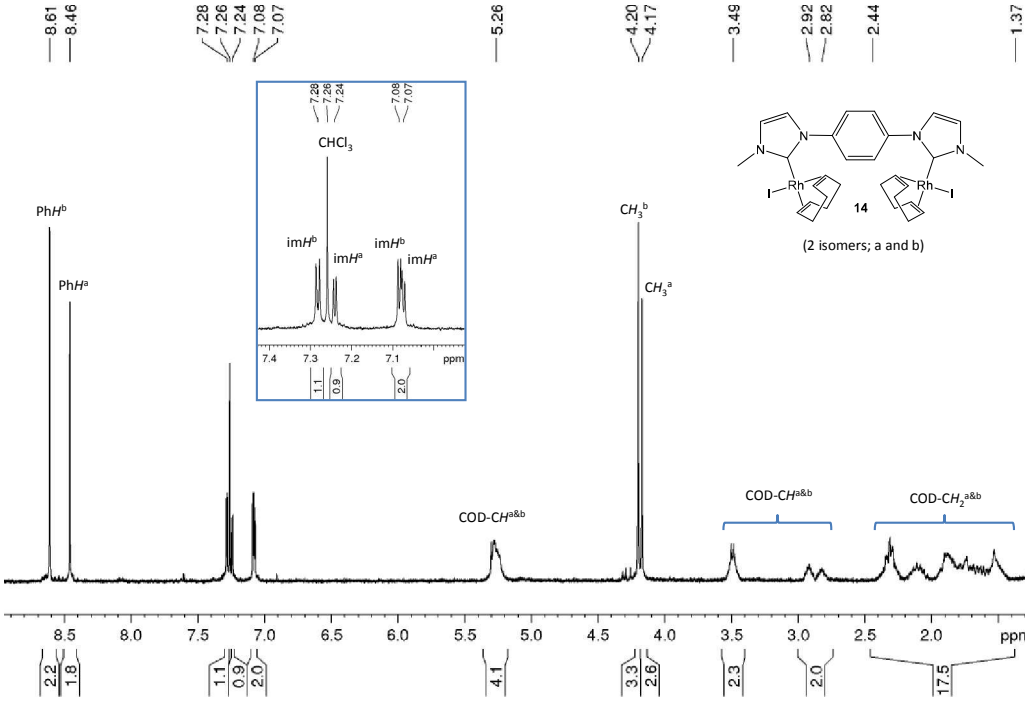


**Figure S12**: κ[2]-*mono*-Rh(COD) (**15**), $^1$H NMR (Acetone-$d_6$, 400 MHz)

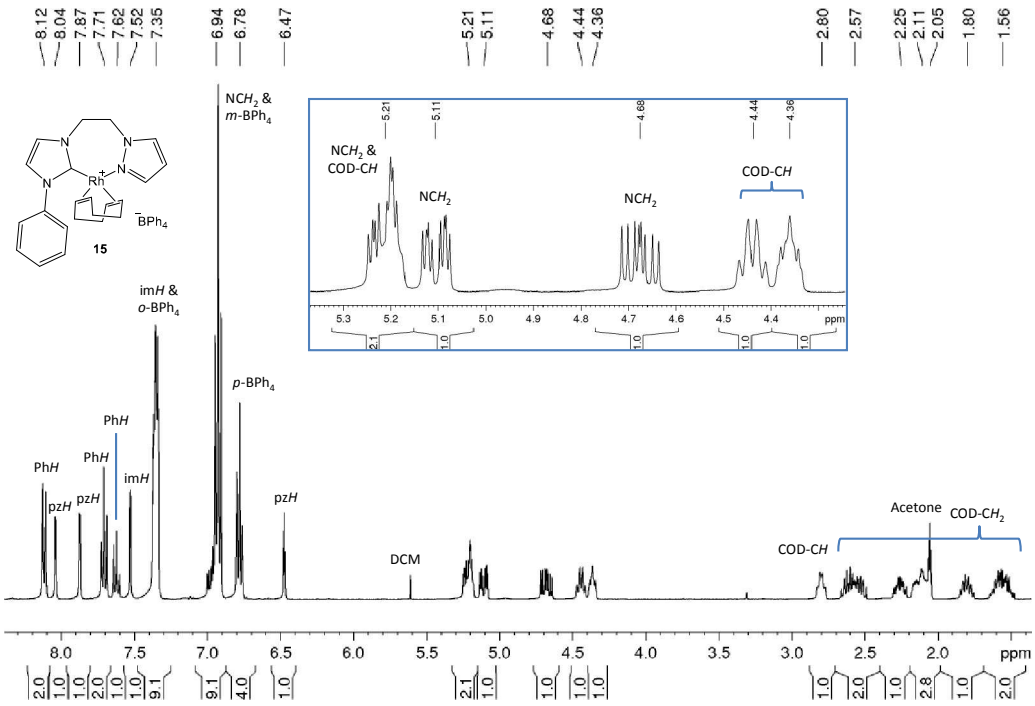

**Figure S13**: κ²-*mono*-Rh(COD) (**15**), $^{13}$C NMR (Acetone-$d_6$, 100 MHz)

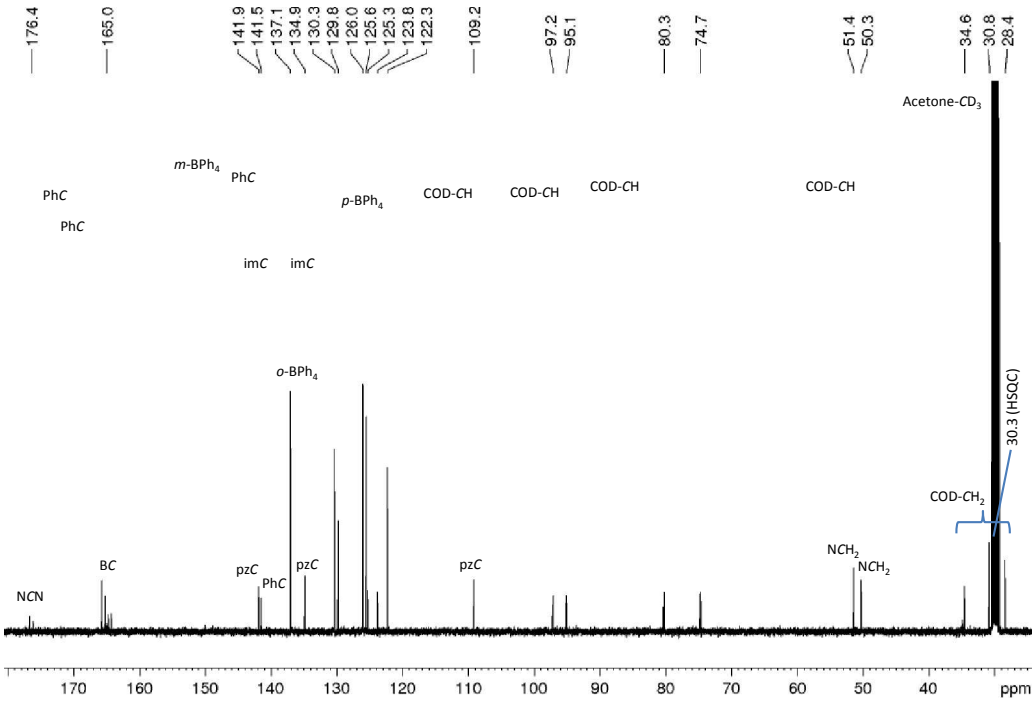


**Figure S14**: κ²-*meta*-Rh(COD) (**16**), $^{1}$H NMR (Acetone-$d_6$, 500 MHz)

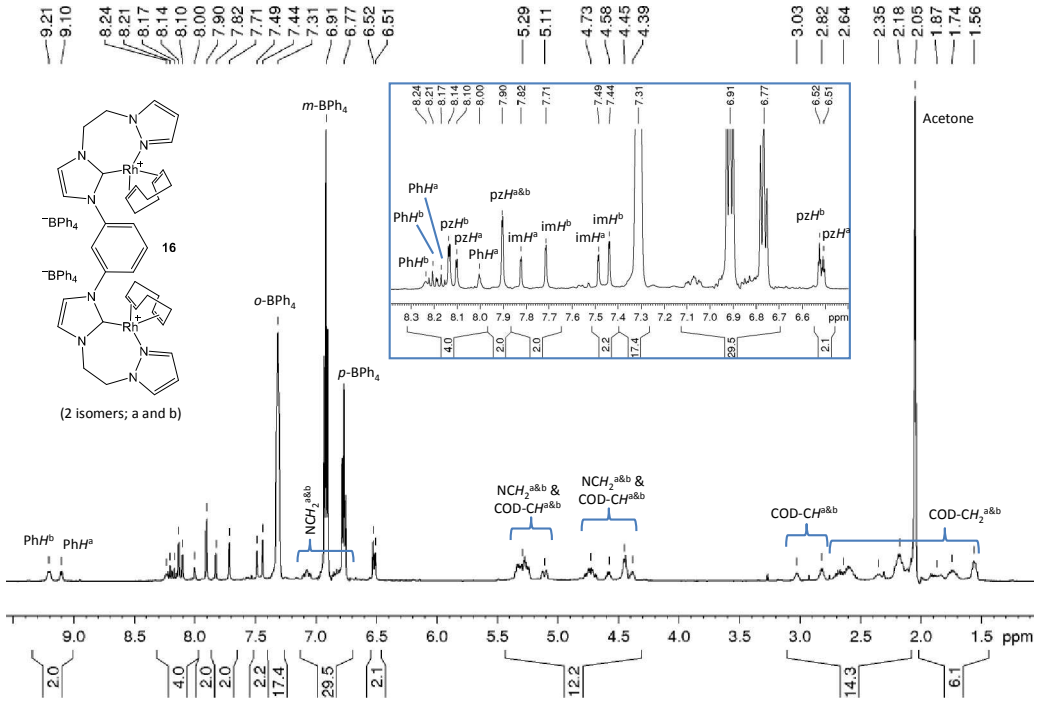

**Figure S15**: $\kappa^2$-*meta*-Rh(COD) (**16**), $^{13}$C NMR (Acetone-$d_6$, 100 MHz)

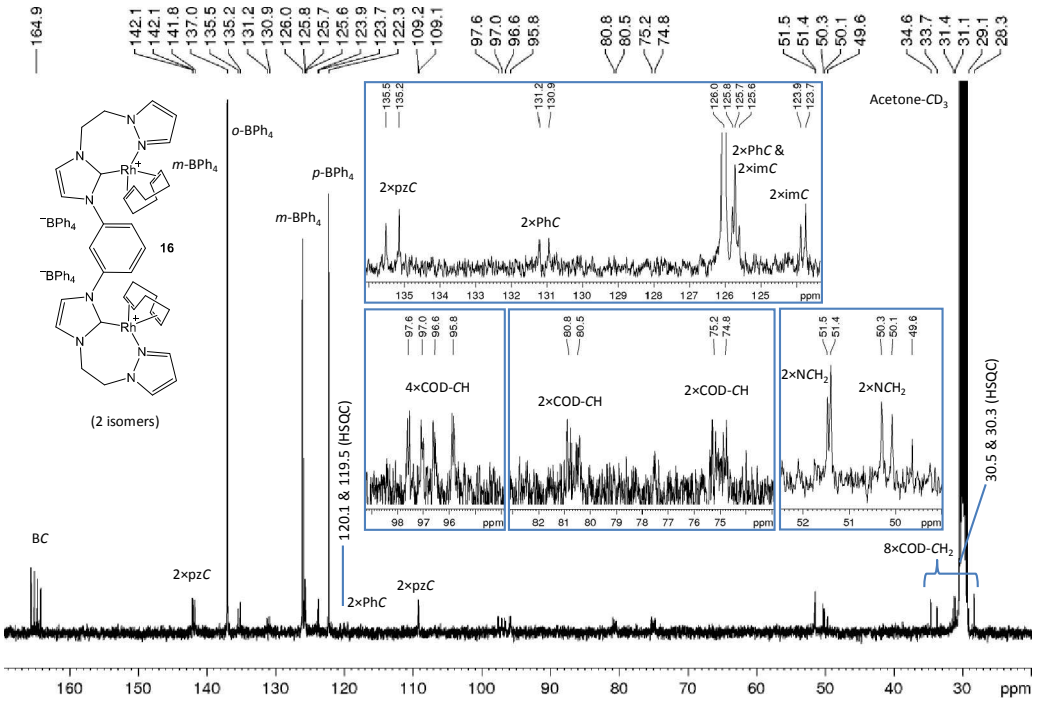


**Figure S16**: $\kappa^1$-*mono*-Rh(CO)$_2$ (**17**), $^1$H NMR ($CDCl_3$, 600 MHz)

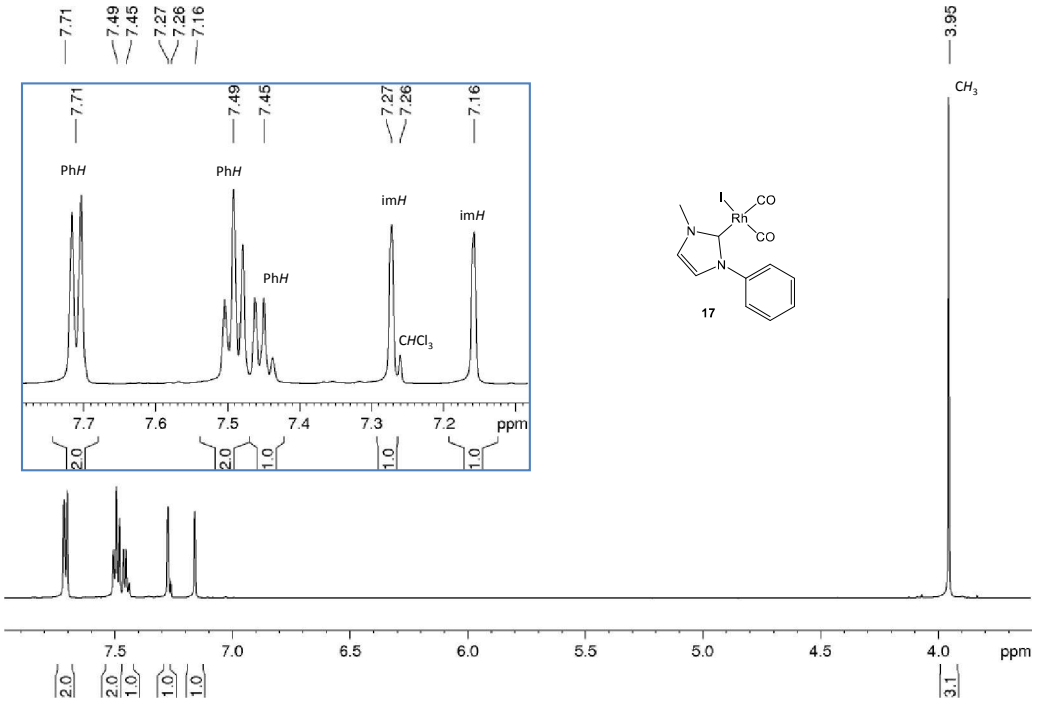

**Figure S17**: $\kappa^1$-*mono*-Rh(CO)$_2$ (**17**), $^{13}$C NMR (CDCl$_3$, 150 MHz)

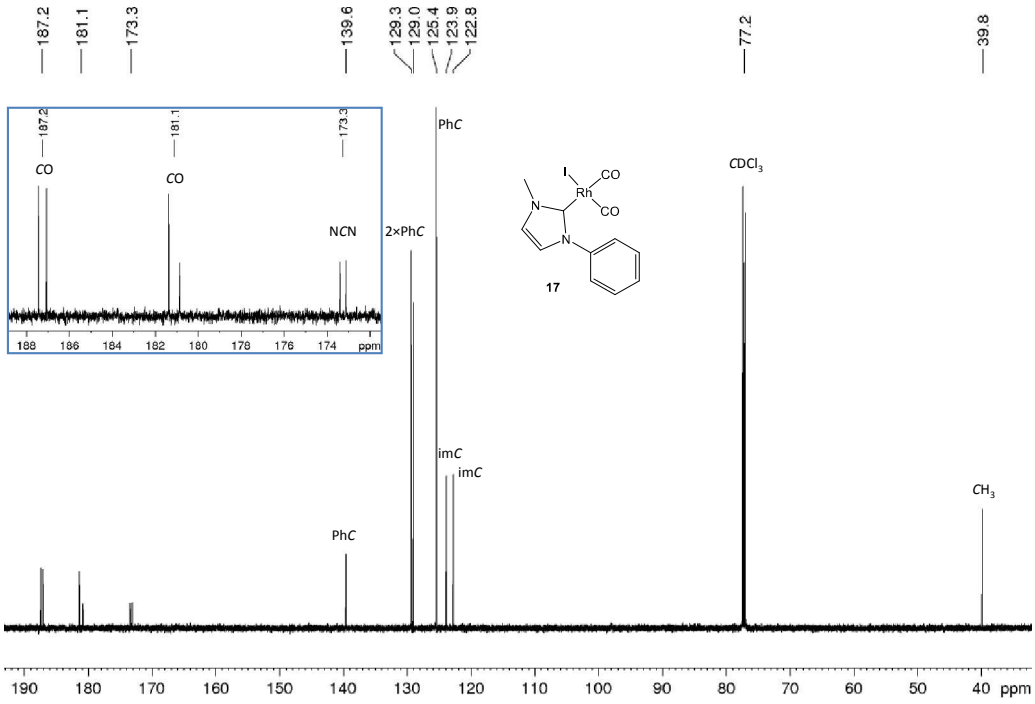


**Figure S18**: $\kappa^1$-*meta*-Rh(CO)$_2$ (**18**), $^1$H NMR (CDCl$_3$, 400 MHz, 250 K)

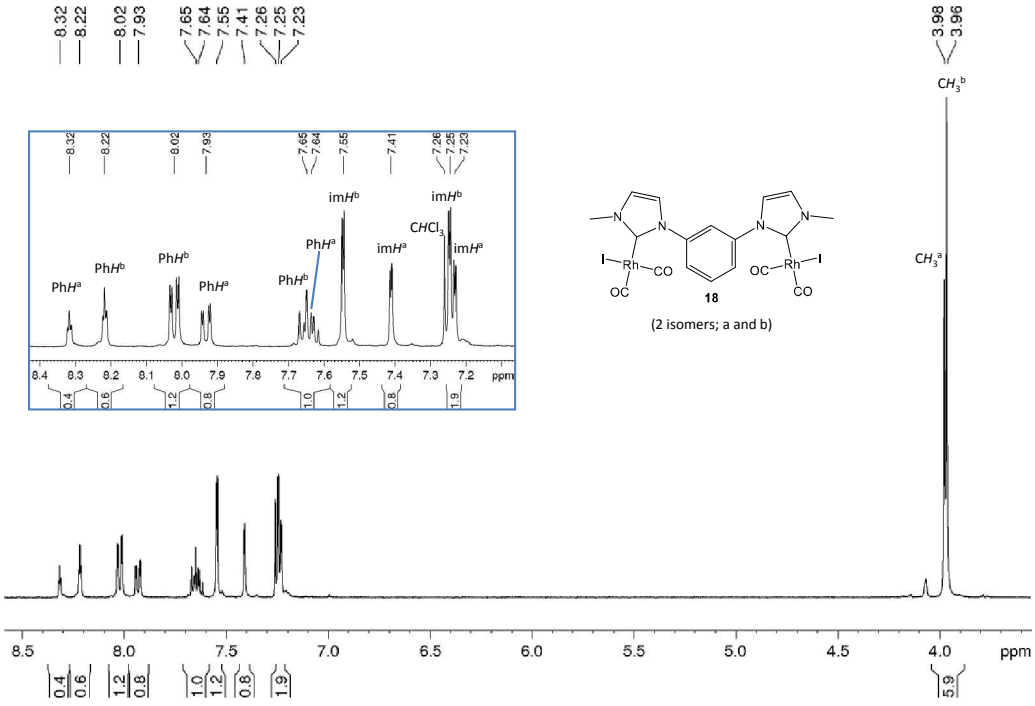

**Figure S19**: $\kappa^1$-*meta*-Rh(CO)$_2$ (**18**), $^{13}$C NMR ($CDCl_3$, 100 MHz, 250 K)

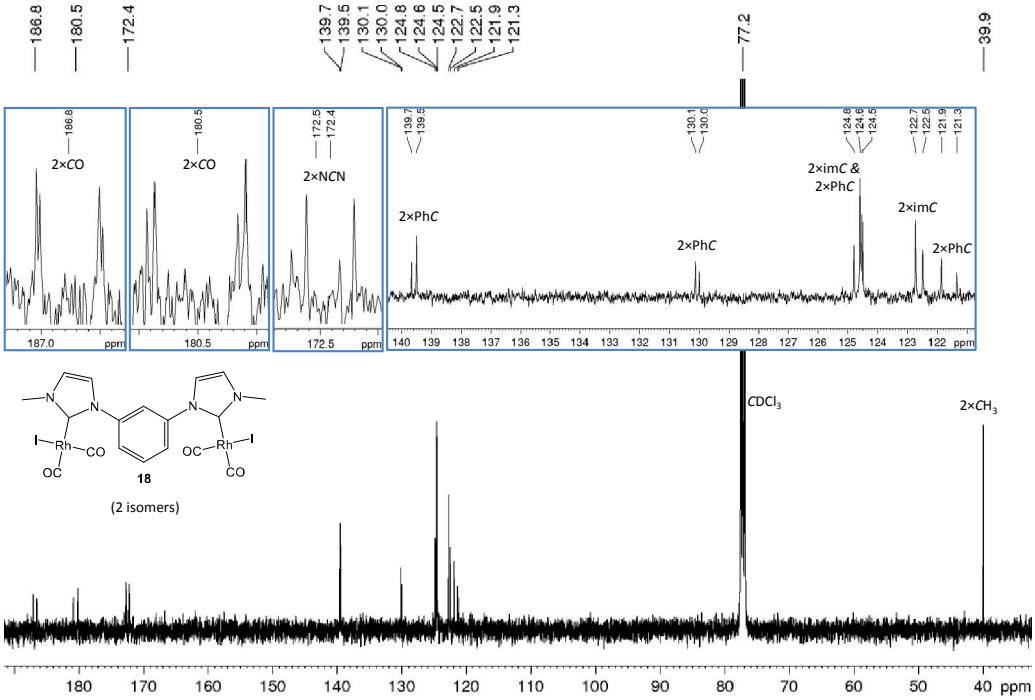


**Figure S20**: $\kappa^1$-*meta*-Rh(CO)$_2$ (**18**), $^1$H NMR ($CDCl_3$); (a) 300 MHz, 298 K, (b) 400 MHz, 250 K.

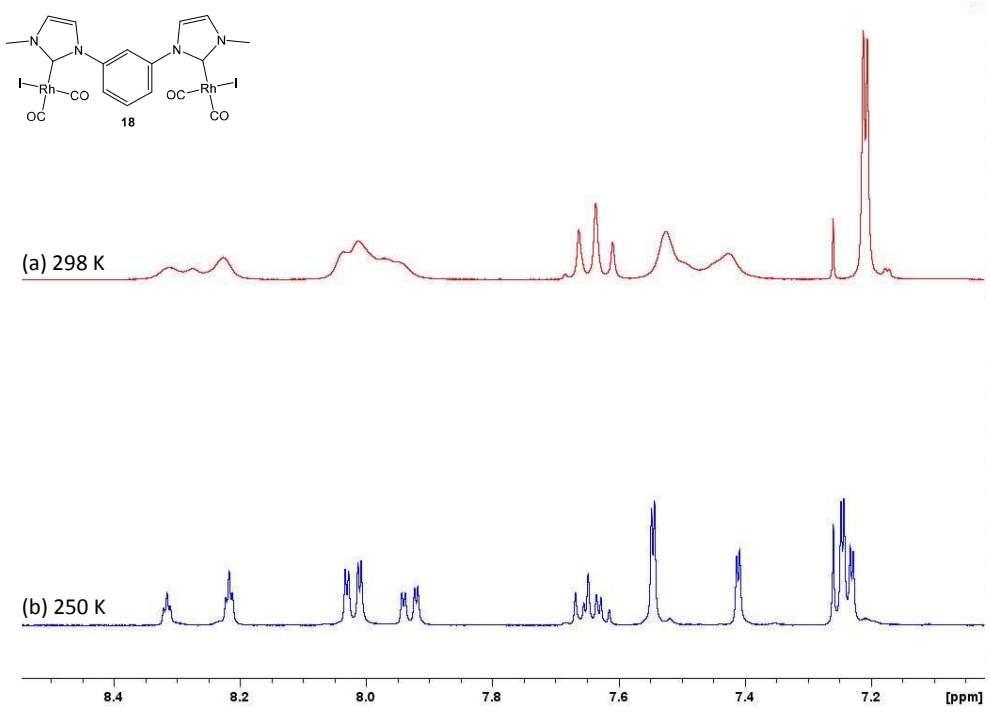

**Figure S21**: κ[1]-*para*-Rh(CO)$_2$ (**19**), $^1$H NMR (CDCl$_3$, 300 MHz)

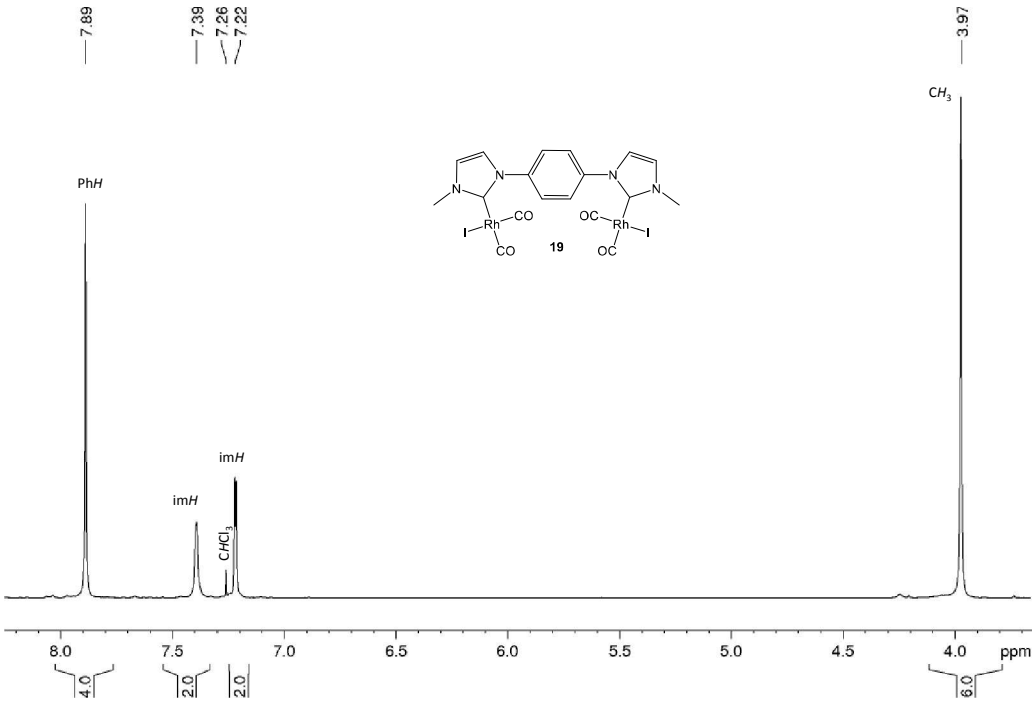


**Figure S22**: κ[1]-*para*-Rh(CO)$_2$ (**19**), $^{13}$C NMR (CDCl$_3$, 75 MHz)

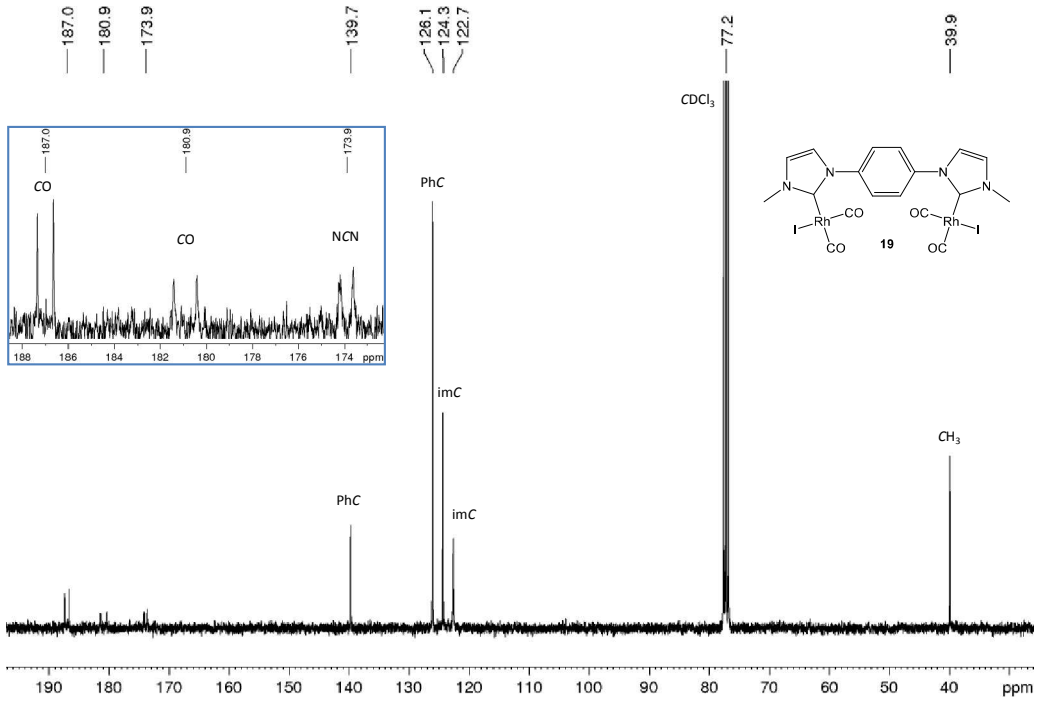

**Figure S23**: κ²-*mono*-Rh(CO)$_2$ (**20**), $^1$H NMR (Acetone-$d_6$, 400 MHz)

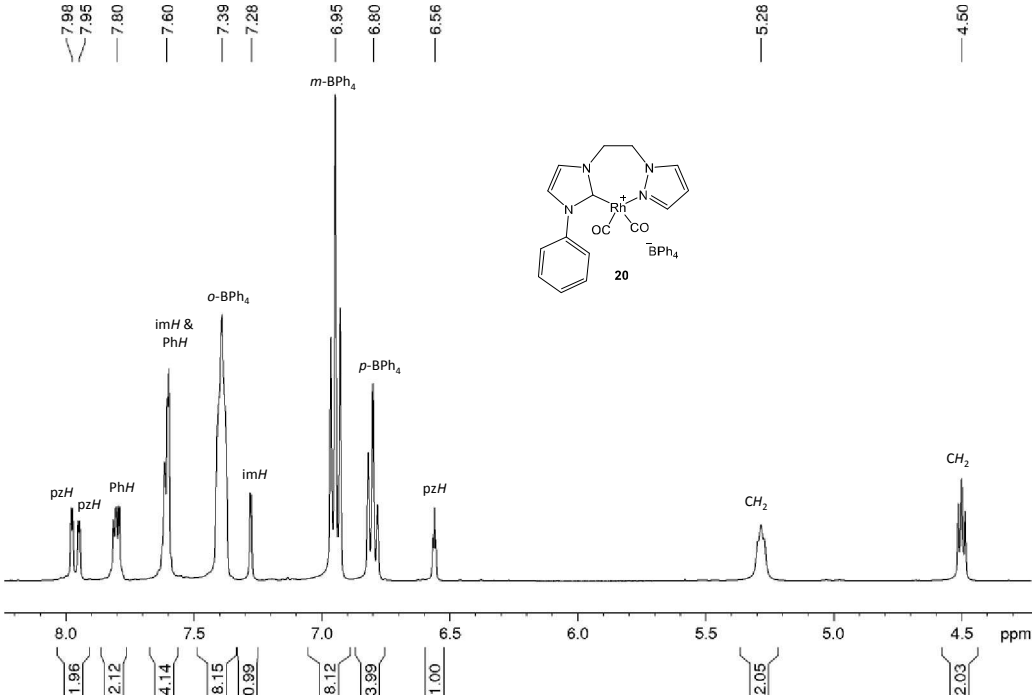


**Figure S24**: κ²-*mono*-Rh(CO)$_2$ (**20**), $^{13}$C NMR (Acetone-$d_6$, 100 MHz)

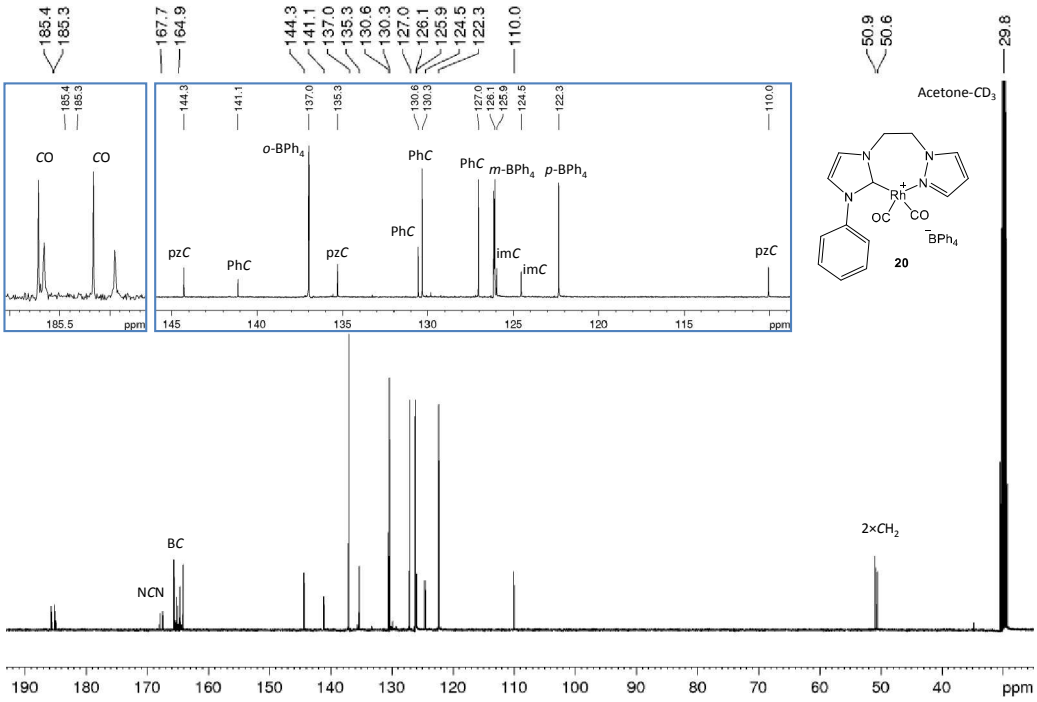

**Figure S25**: κ²-*meta*-Rh(CO)$_2$ (**21**), $^1$H NMR (Acetone-$d_6$, 400 MHz)

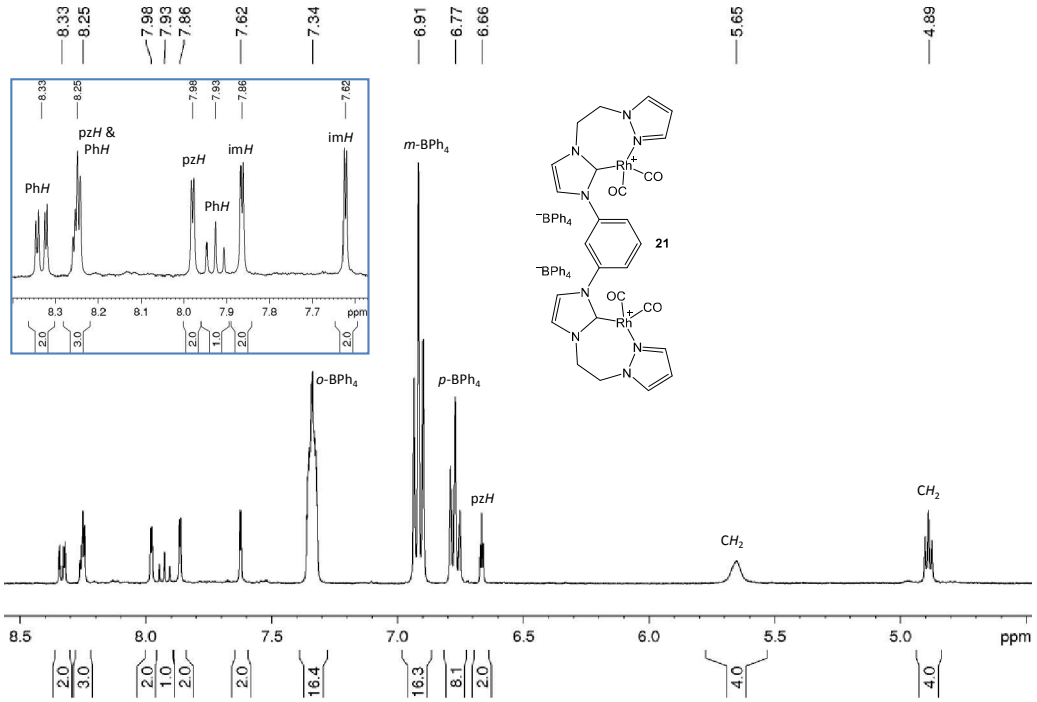


**Figure S26**: κ²-*meta*-Rh(CO)$_2$ (**21**), $^{13}$C NMR (Acetone-$d_6$, 100 MHz)

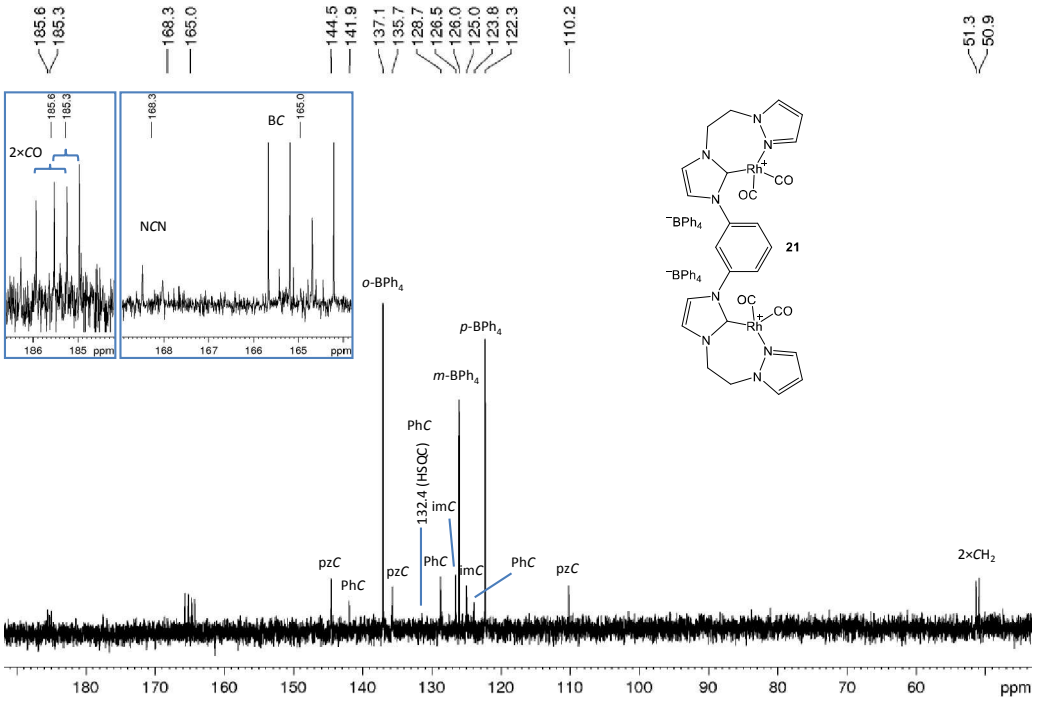

**Figure S27**: Dihydroalkoxylation reaction mixture, $^{1}$H NMR (TCE-$d_2$, 500 MHz)

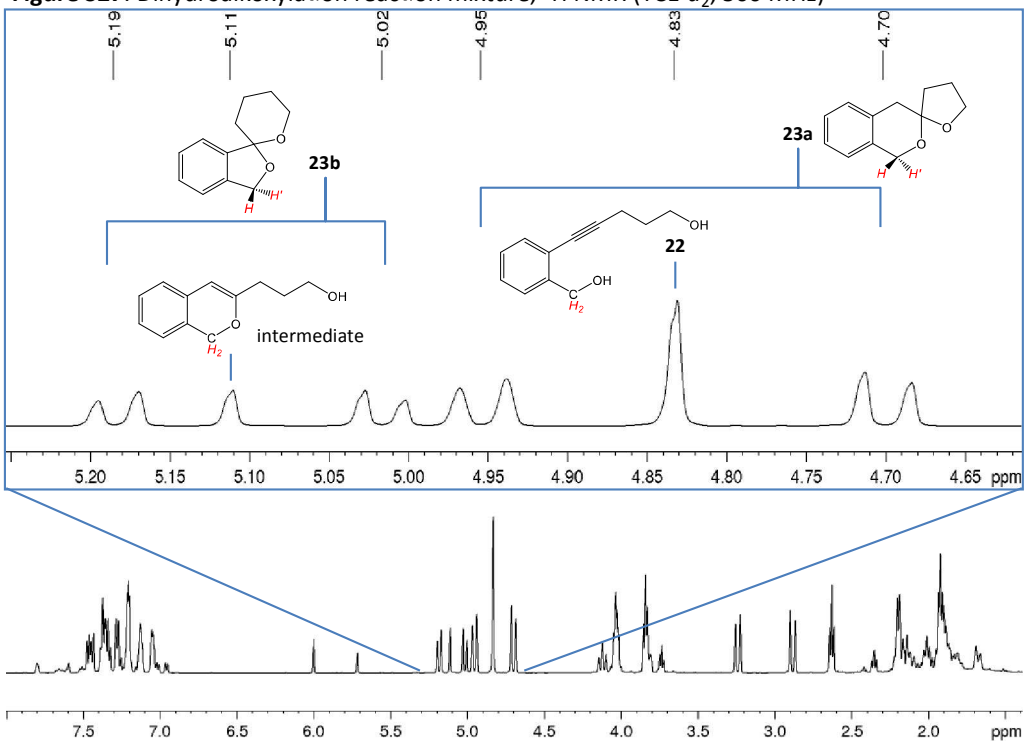


**Figure S28**: Hydrosilylation reaction mixture, $^{1}$H NMR (THF-$d_8$, 500 MHz)