Electronic Supplementary Information (ESI) for:

Reversible CO_2 Binding Triggered by Metal-Ligand Cooperation in a Rhenium(I) PNP Pincer-Type Complex and the Reaction with Dihydrogen.

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1. NMR Spectra

1.1 NMR spectra of [Re(PNP^{tBu}-COO)(CO)$_2$] (**3**).

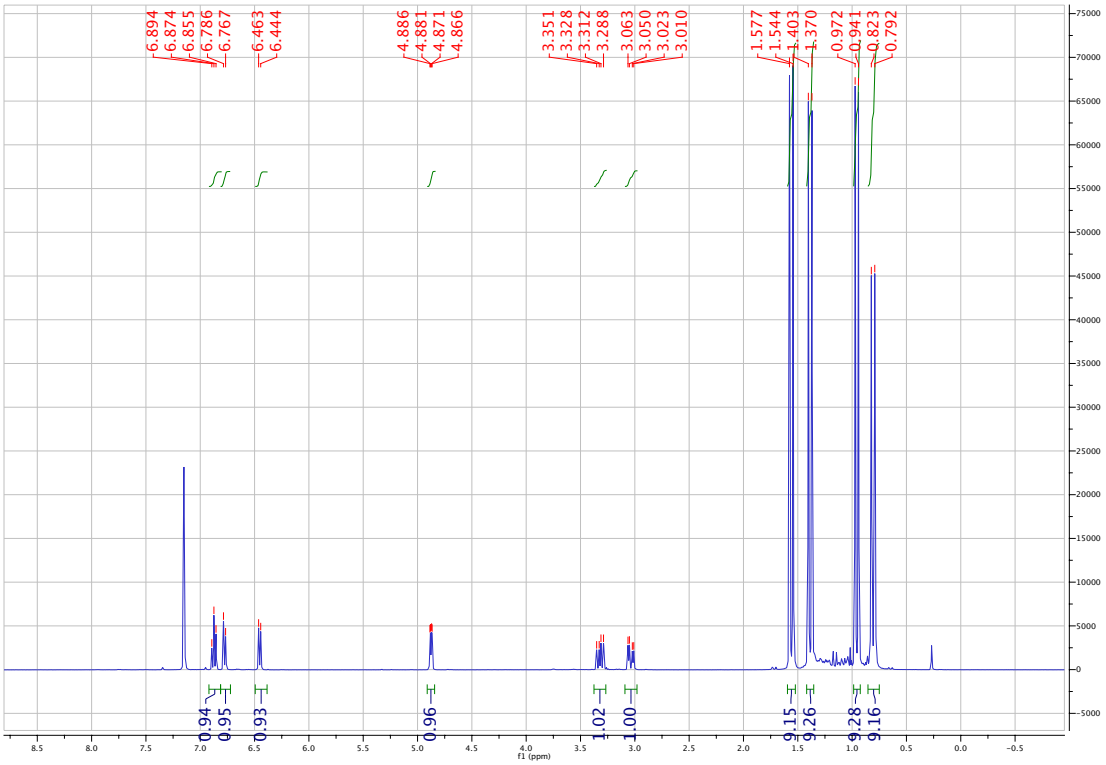

Figure S1: ^{1}H NMR spectrum (400.36 MHz C_6D_6, 25°C) of complex **3**.

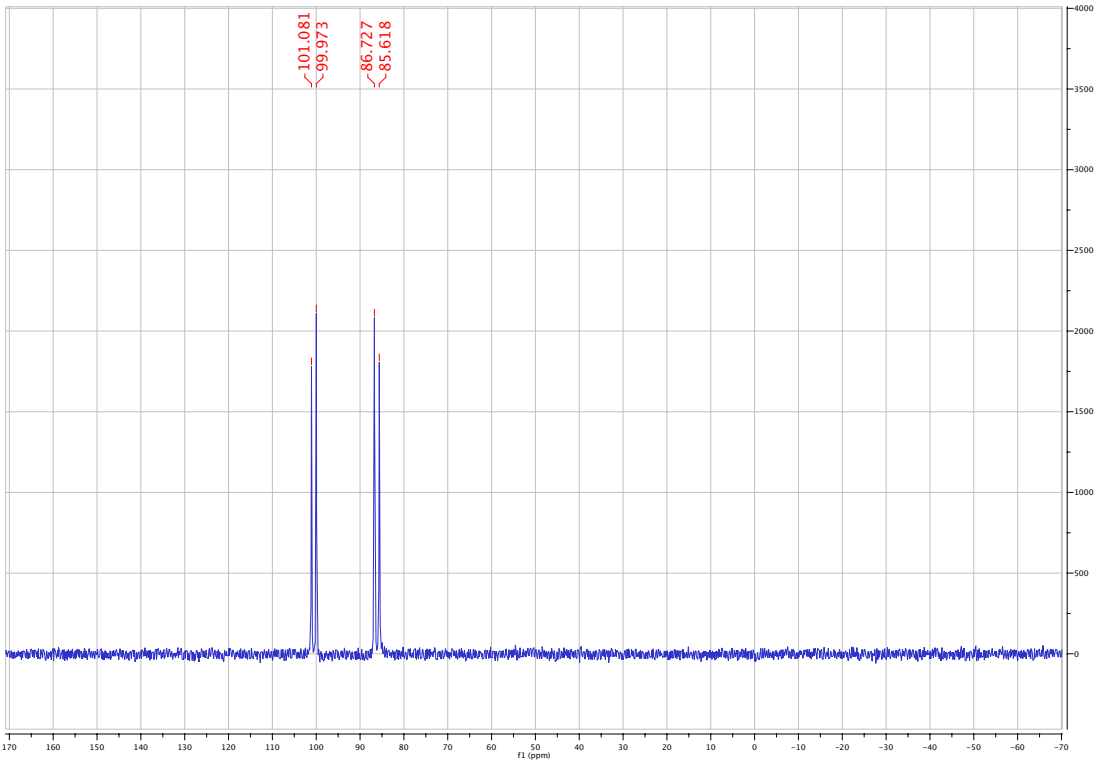

Figure S2: ^{31}P{^{1}H} NMR spectrum (121.5 MHz, CD_2Cl_2, 25°C) of complex **3**.

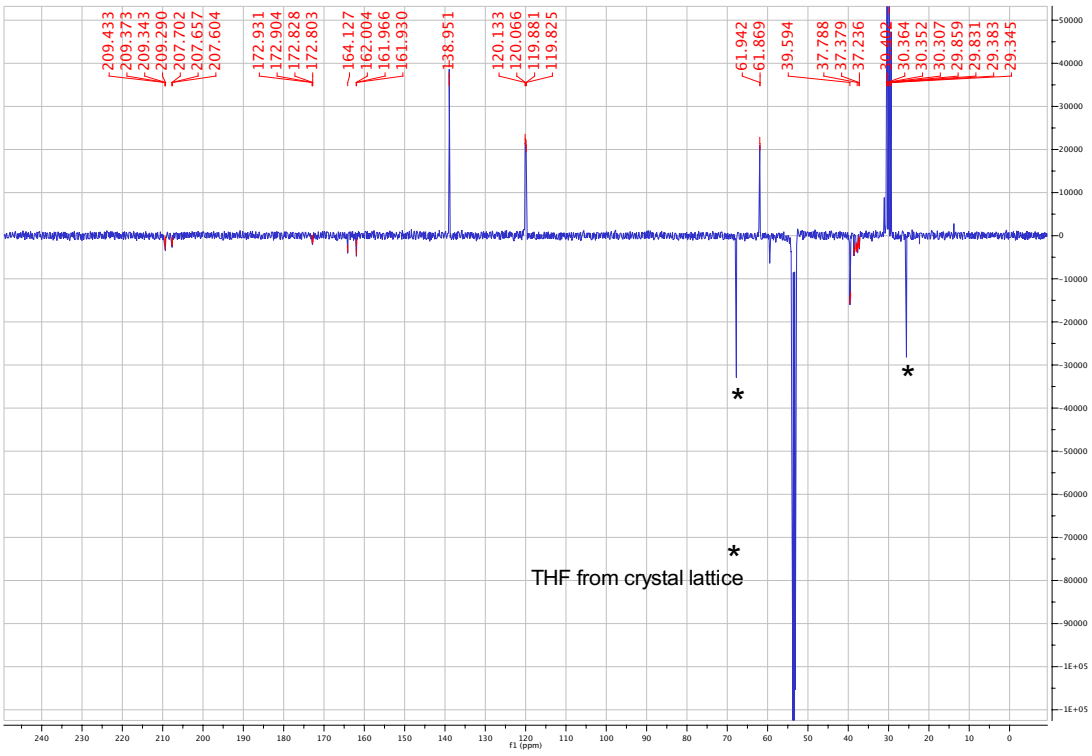

Figure S3: $^{13}C\{^{1}H\}$ QDEPT NMR spectrum (100.7 MHz C_6D_6, 25°C) of complex **3**.

1.2 NMR spectra of [Re(PNP^{tBu}-^{13}COO)(CO)$_2$] (**3a**).

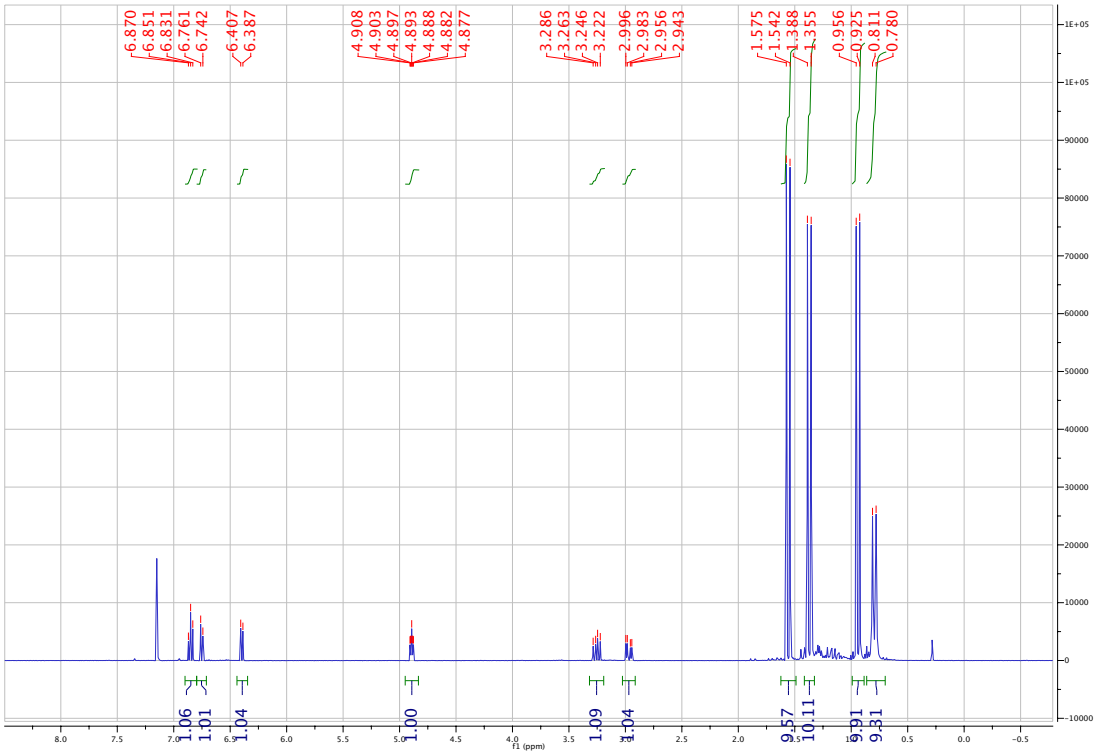

Figure S4: ^{1}H NMR spectrum (400.36 MHz C_6D_6, 25°C) of complex **3a**.

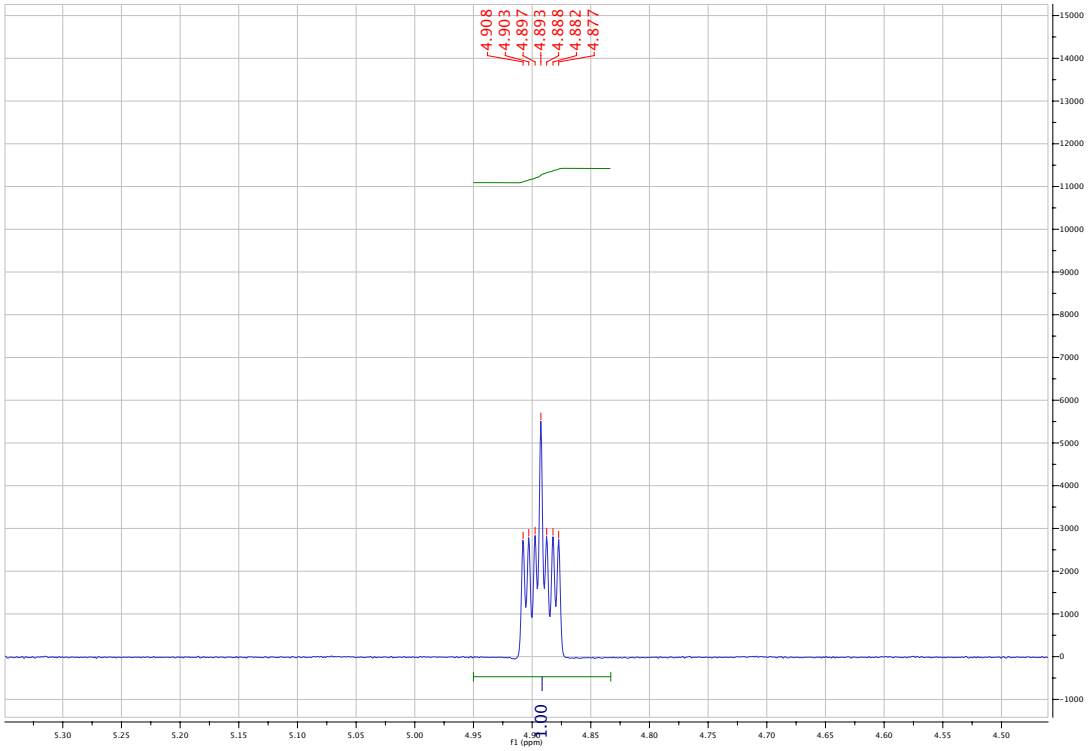

Figure S5: Magnification of ^{1}H NMR spectrum (400.36 MHz C_6D_6, 25°C, methylene CH_2 arm) of complex **3a.**

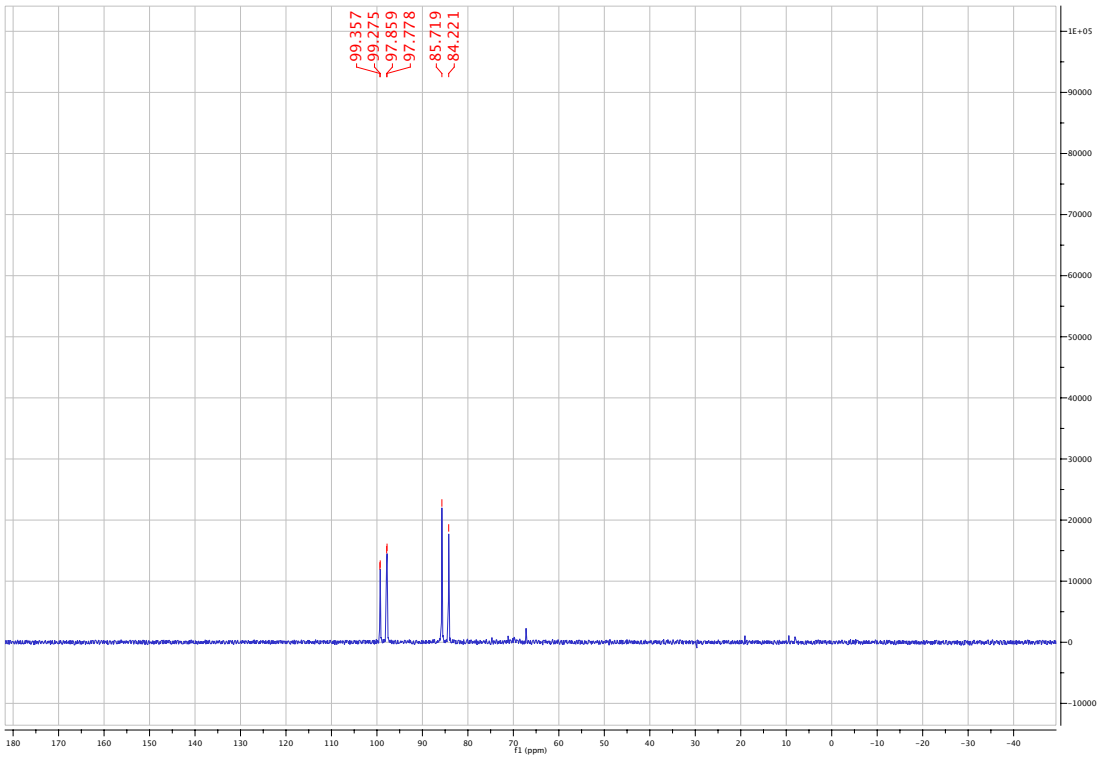

Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum (121.5 MHz, C_6D_6, 25°C) of complex **3a.**

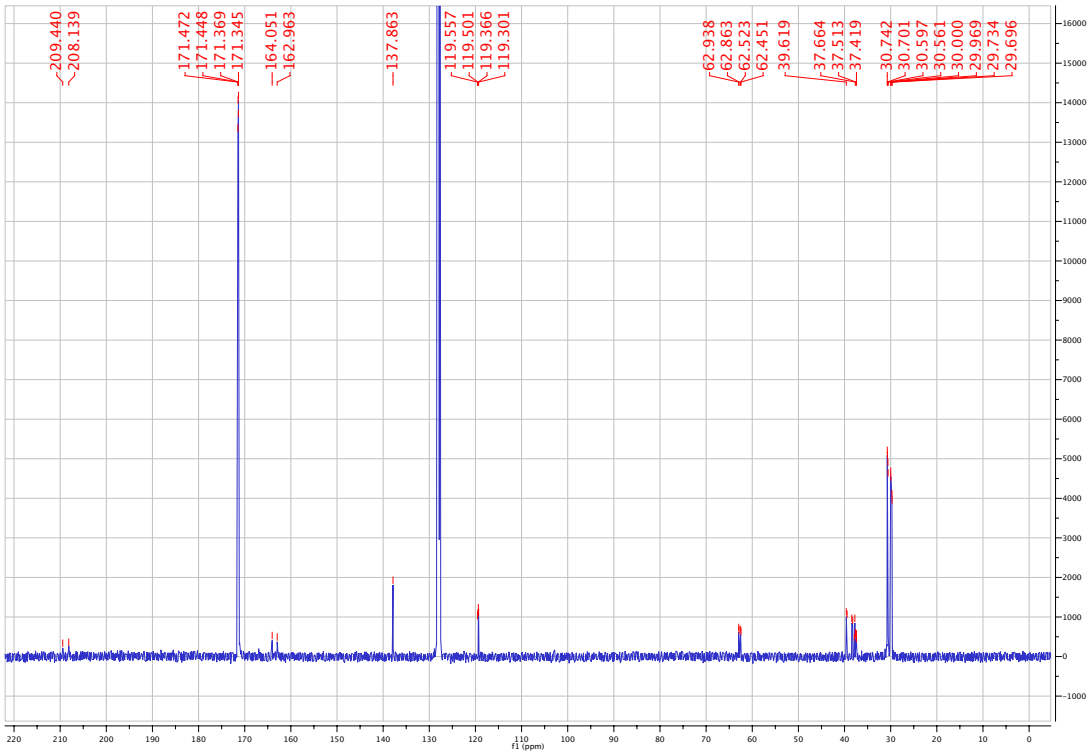

Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz C_6D_6, 25°C) of complex **3a**.

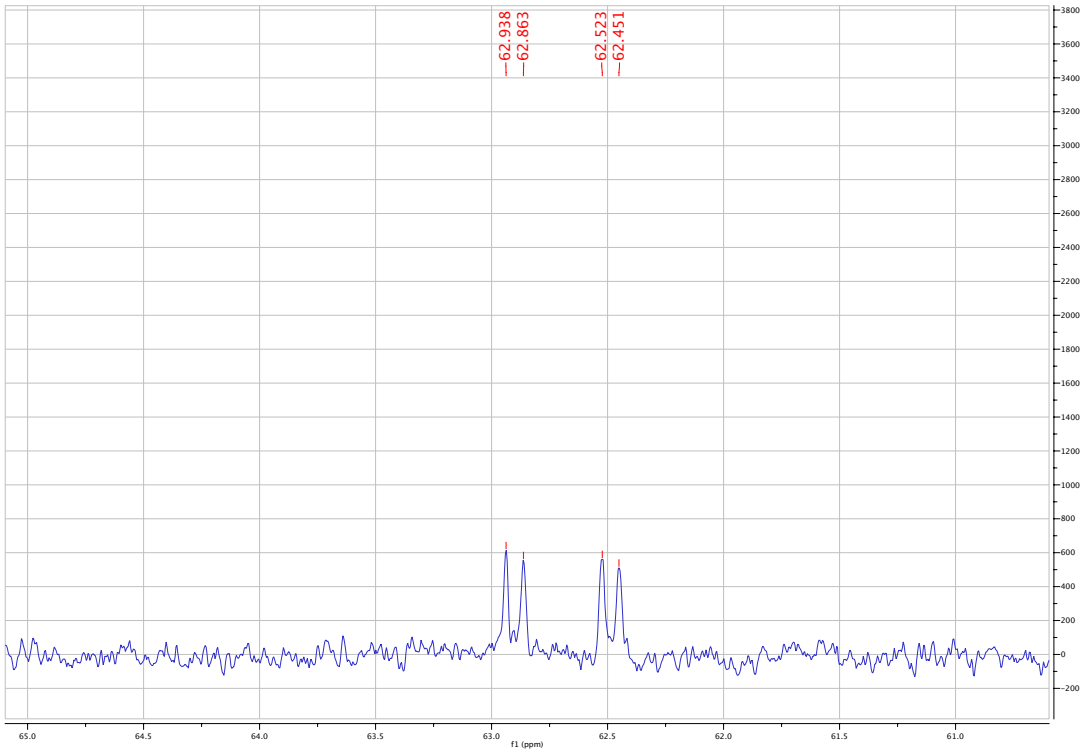

Figure S8: Section of $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz C_6D_6, 25°C, *C*H-^{13}COO moiety) of complex **3a**.

1.3 NMR spectra of [Re(PNP^{tBu})(CO)$_2$H] (**4**).

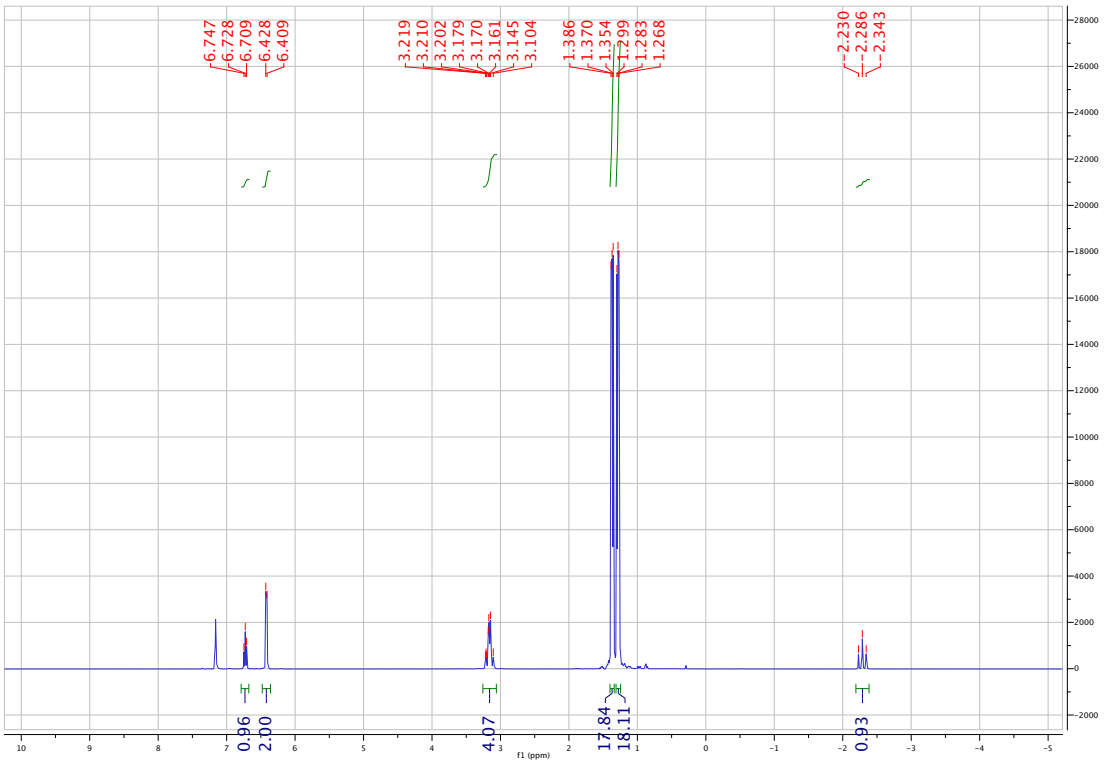

Figure S9: ^{1}H NMR spectrum (400.36 MHz C_6D_6, 25°C) of complex **4**.

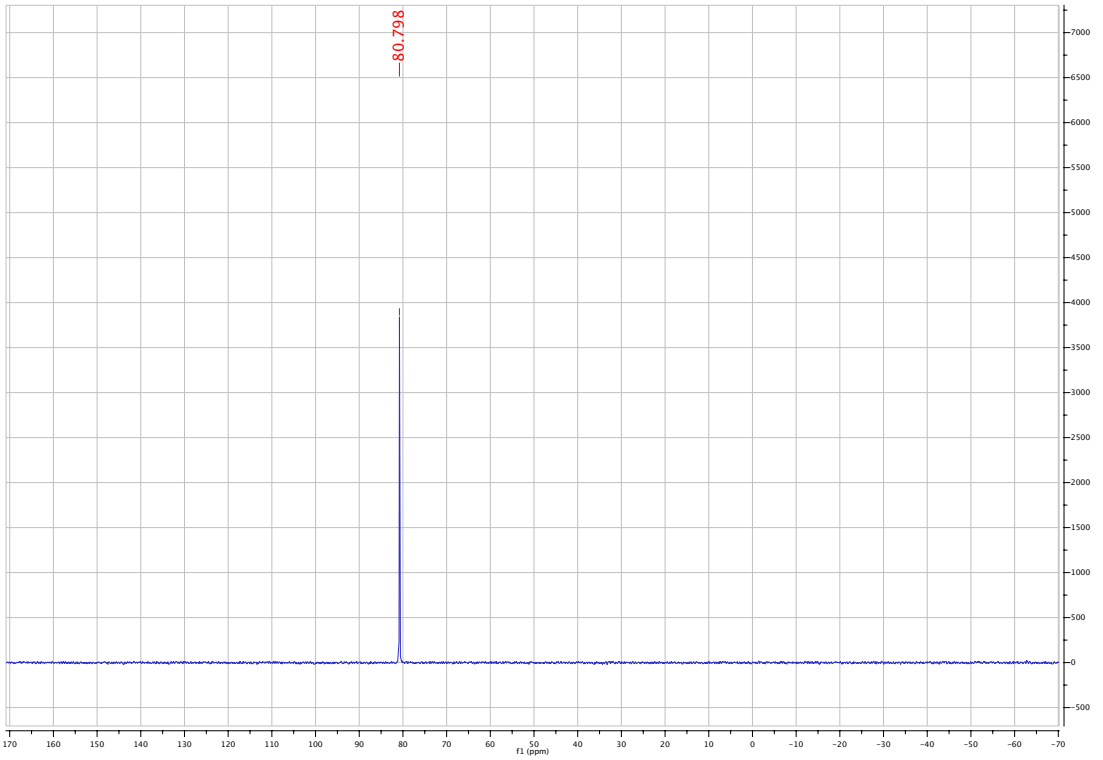

Figure S10: ^{31}P{^{1}H} NMR spectrum (162.1 MHz, C_6D_6, 25°C) of complex **4**.

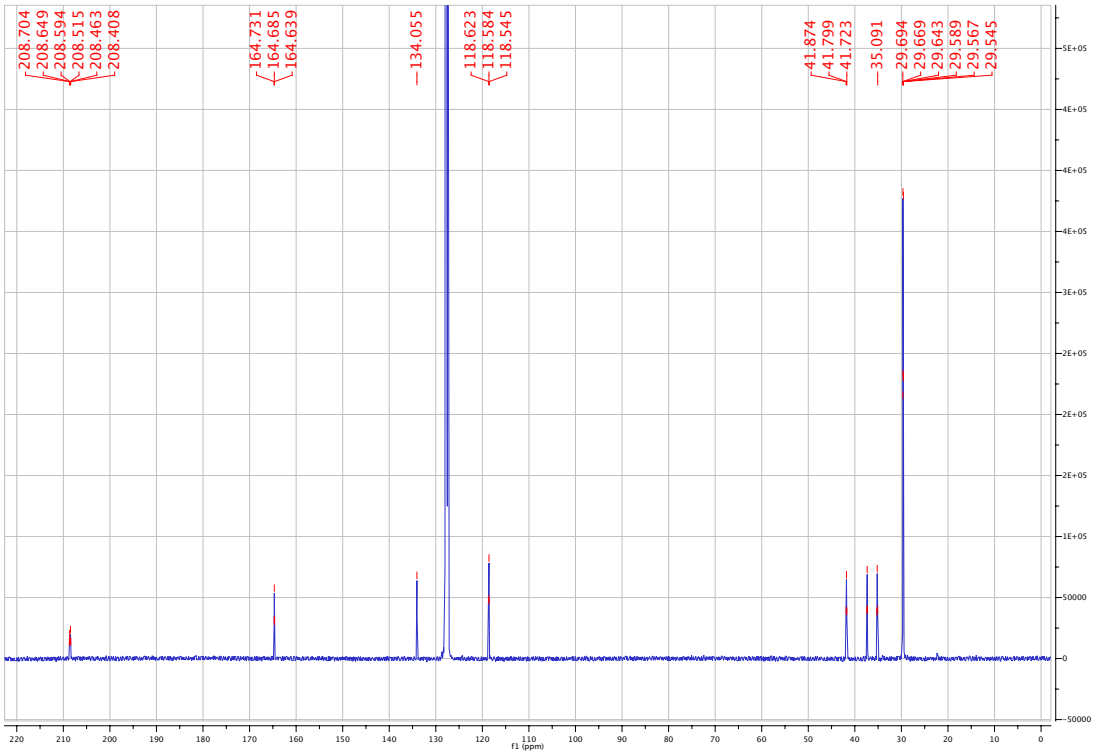

Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum (100.7 MHz C_6D_6, 25°C) of complex **4**.

1.4 NMR spectra of [Re(PNP^{tBu})(CO)$_2$(D)] (**4a**).

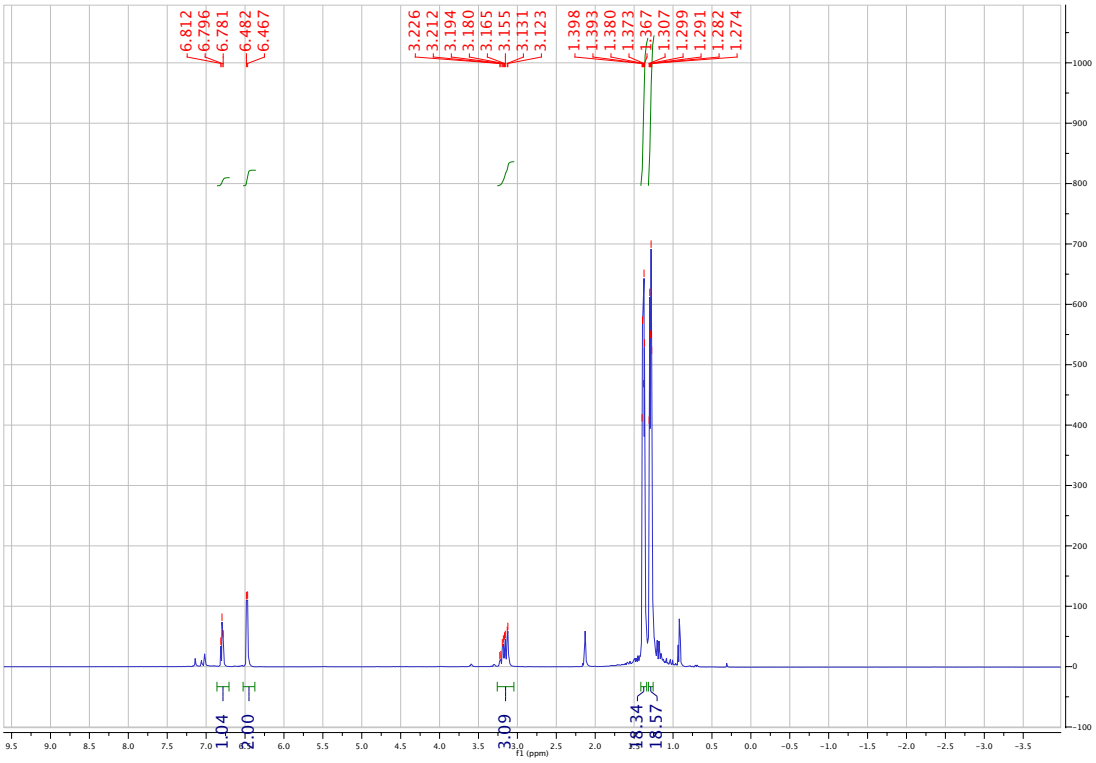

Figure S12: ^{1}H NMR spectrum (500.13 MHz, toluene-d_8, 25°C) of complex **4a.**

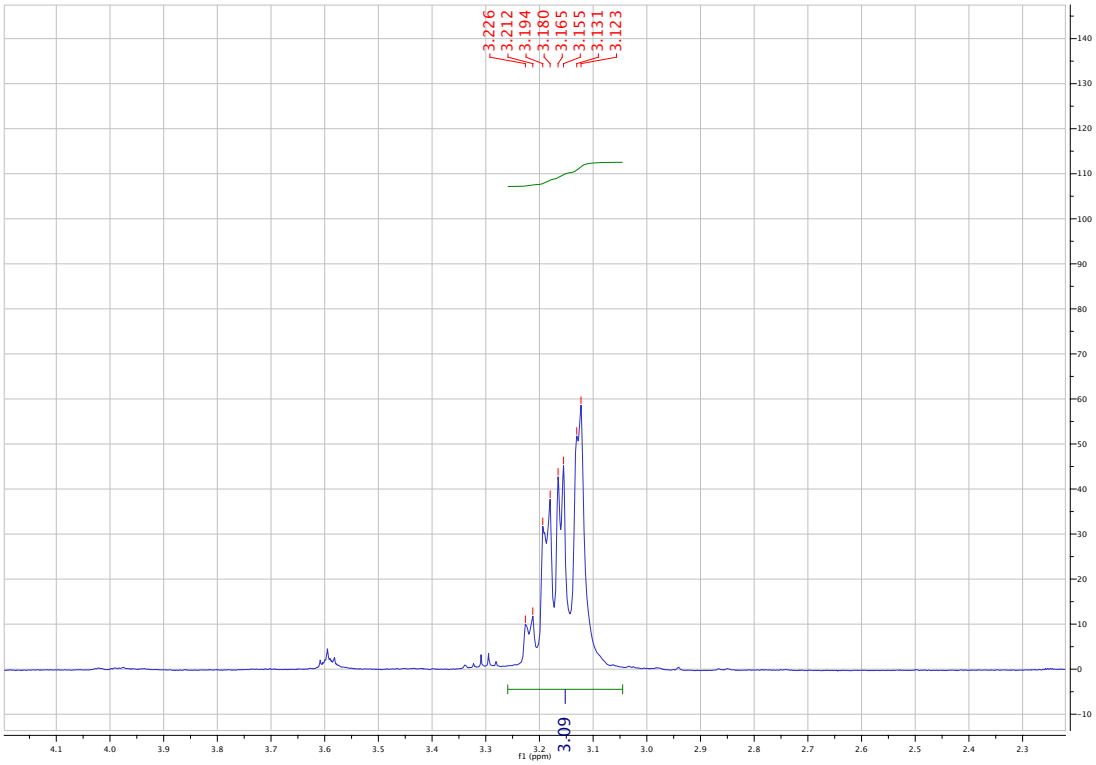

Figure S13: Section of the ^{1}H NMR spectrum (500.13 MHz, toluene-d_8, 25°C, CH_2(D) methylene resonance) of complex **4a.**

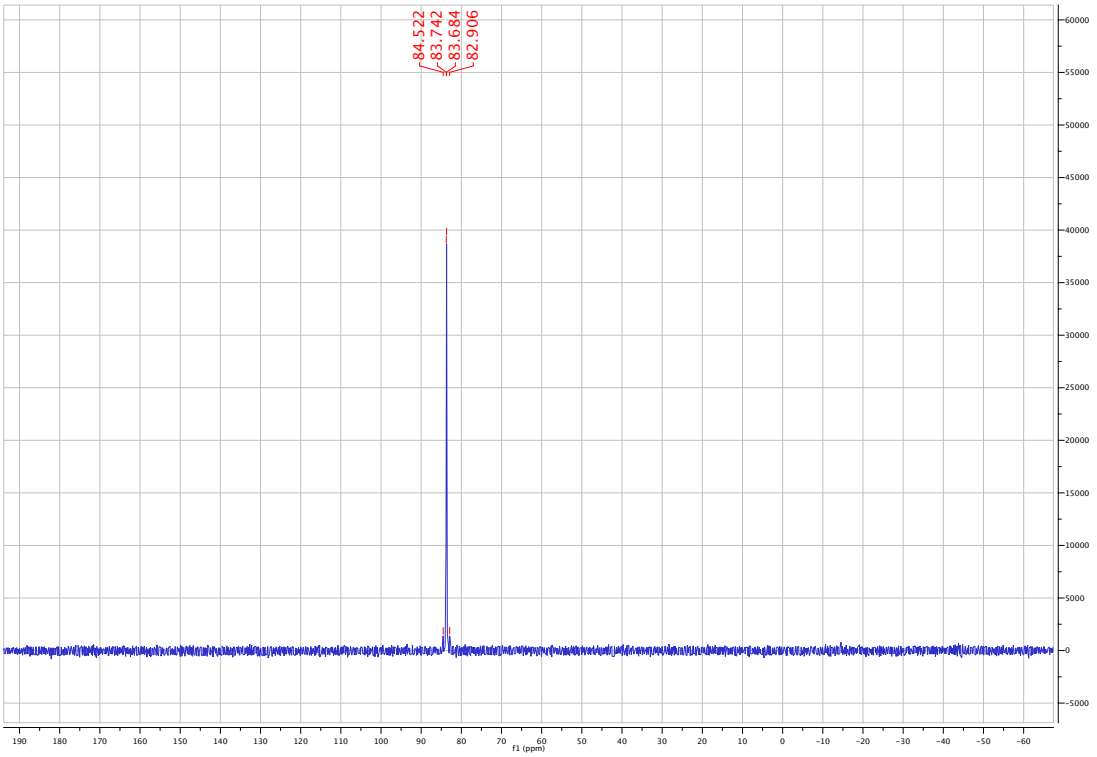

Figure S14: $^{31}P\{^{1}H\}$ NMR spectrum (202.5 MHz,toluene-d_8, 25°C) of complex **4a**.

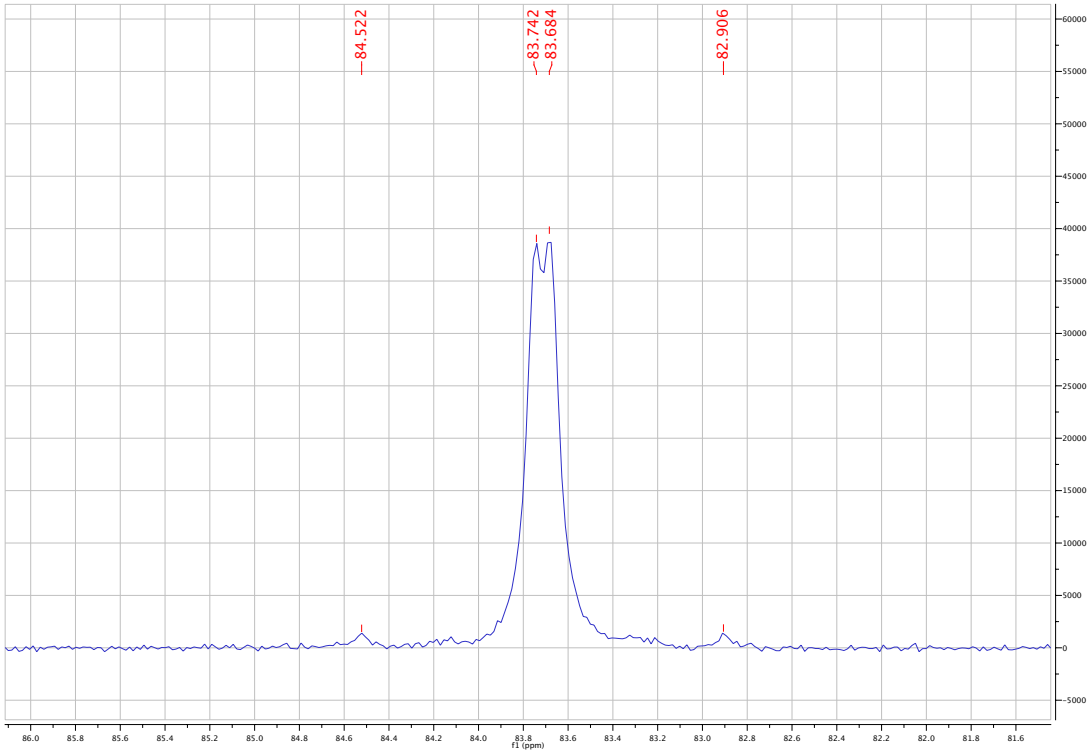

Figure S15: Magnification of $^{31}P\{^{1}H\}$ NMR spectrum (202.5 MHz,toluene-d_8, 25°C) of complex **4a**.

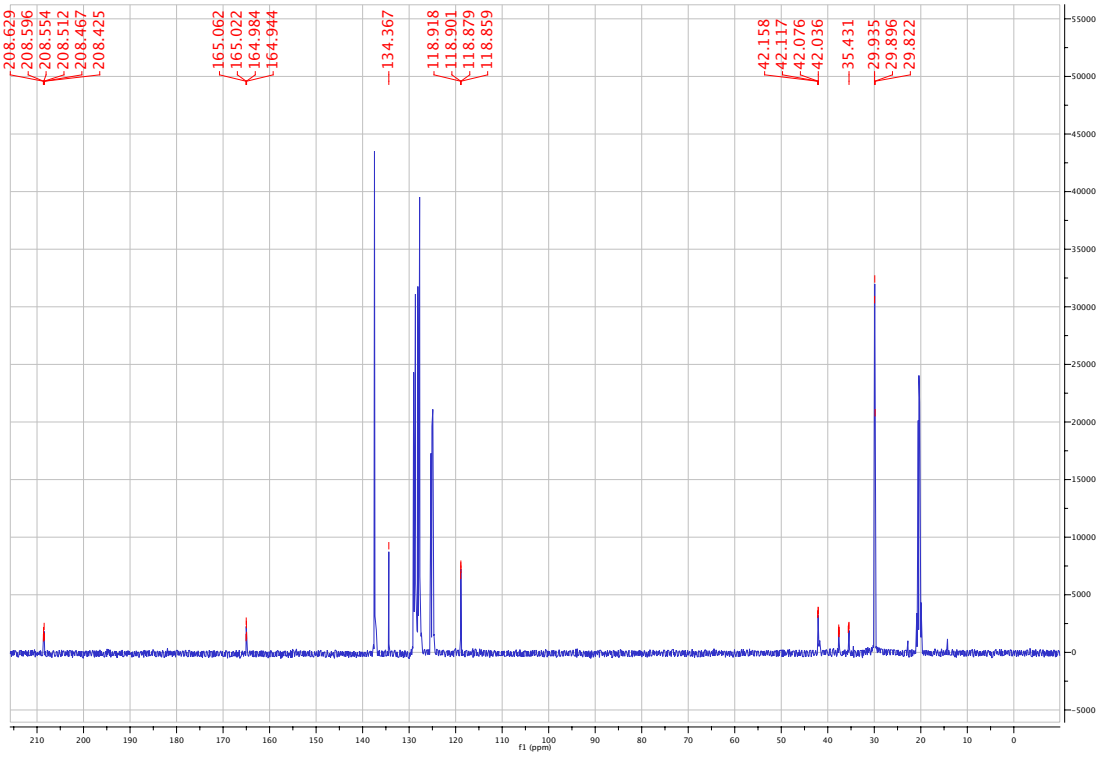

Figure S16: $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, toluene-d_8, 25°C) of complex **4a**.

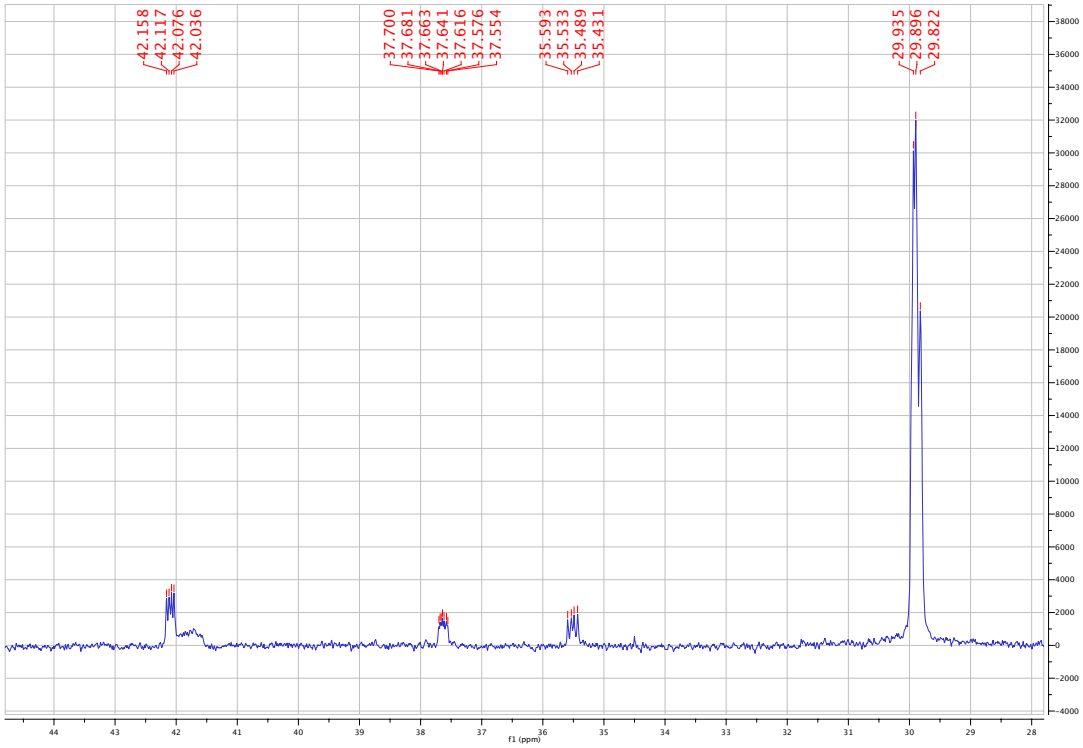

Figure S17: Section of $^{13}C\{^{1}H\}$ NMR spectrum (125.8 MHz, toluene-d_8, 25°C) of complex **4a**.

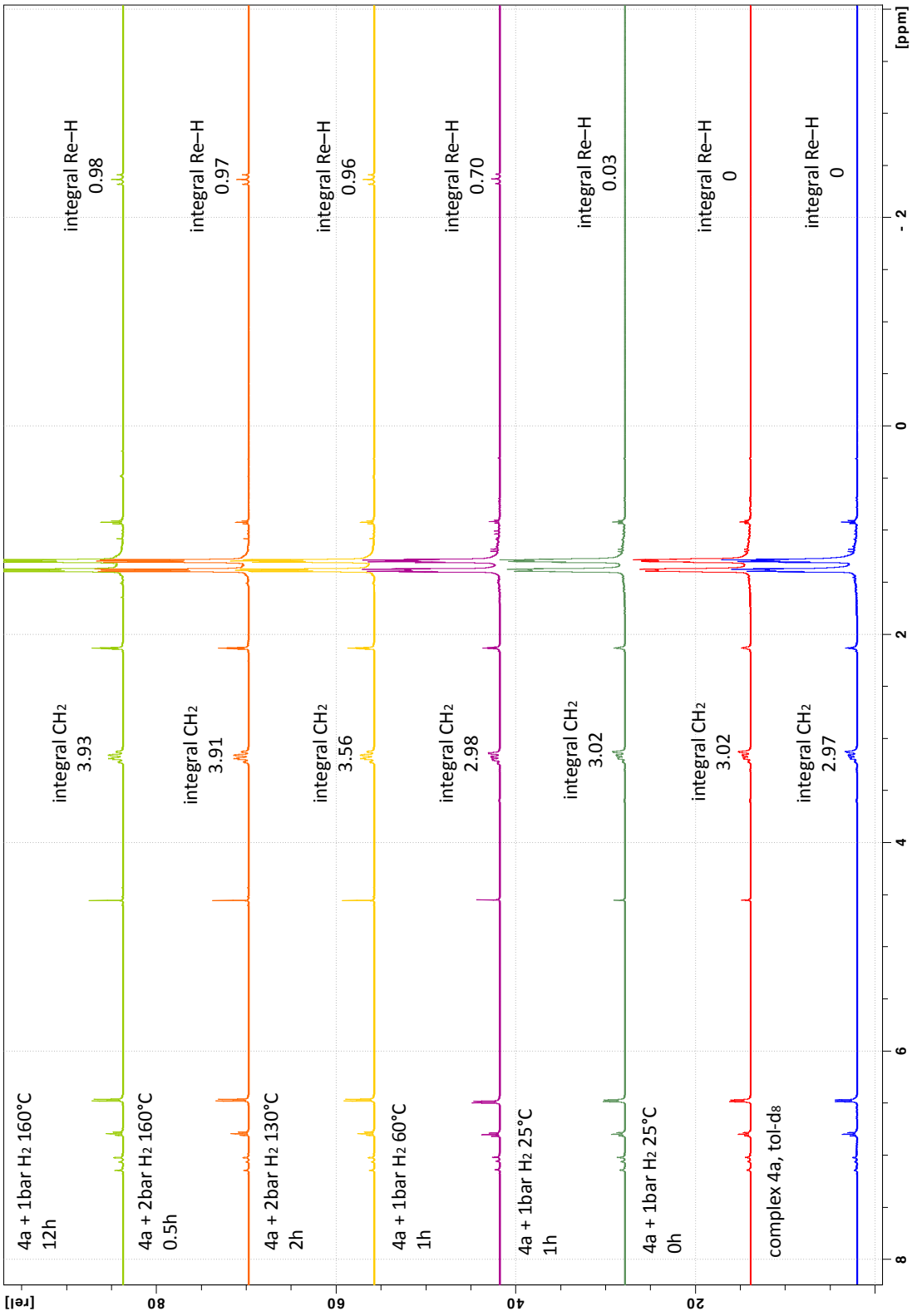

Figure S18: Stacked ^{1}H NMR spectra (500.13 MHz, toluene-d_8) of complex **4a** under variable H_2 pressure and temperature conditions to form **4**. H/D exchange occurs only in Re–D/H moiety at lower temperatures, while CHD is exchanged exclusively at elevated temperature.

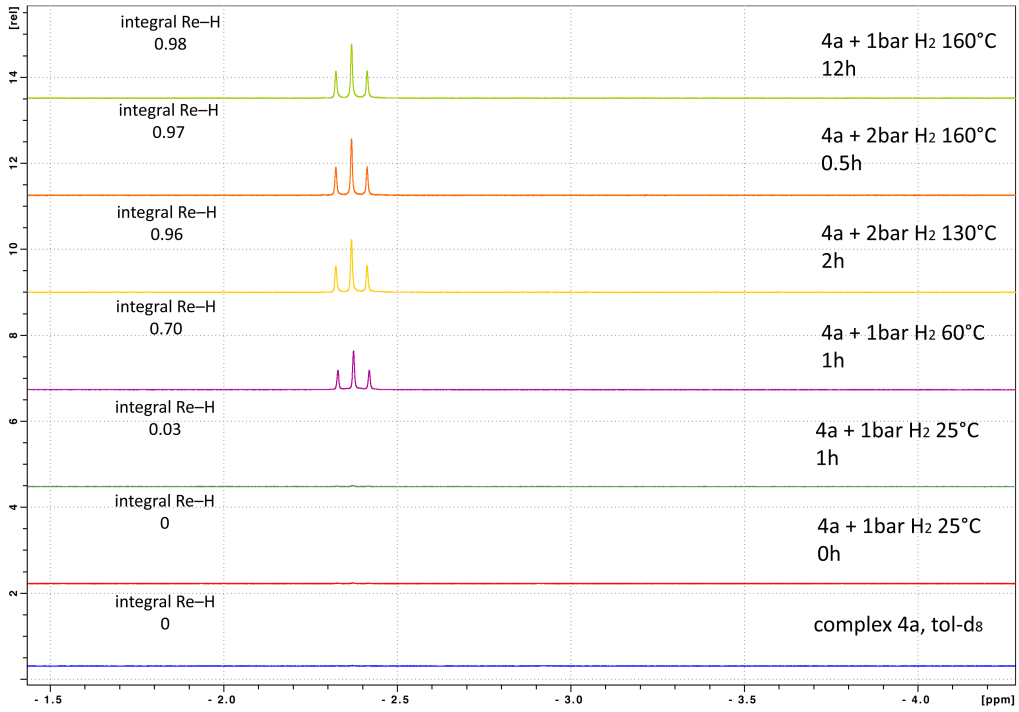

Figure S19: Section of stacked ^{1}H NMR spectra (500.13 MHz, toluene-d_8) of the hydride resonance of complex **4a** under variable H_2 pressure and temperature.

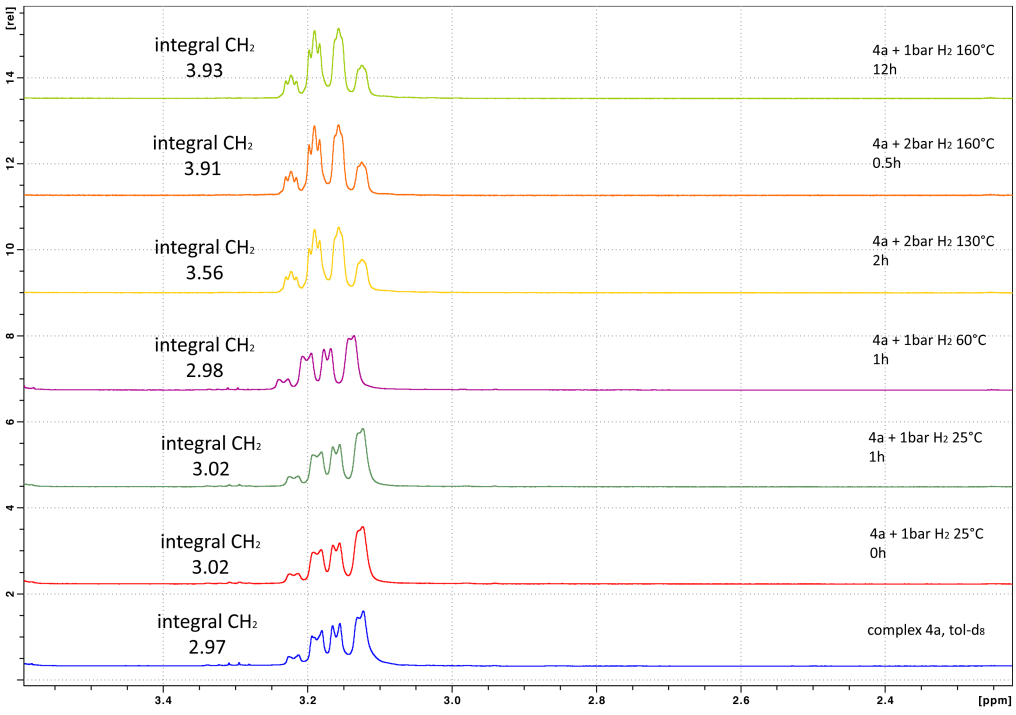

Figure S20: Section of stacked ^{1}H NMR spectra (500.13 MHz, toluene-d_8) of the pincer arm methylene resonances of complex **4a** under variable H_2 pressure and temperature.

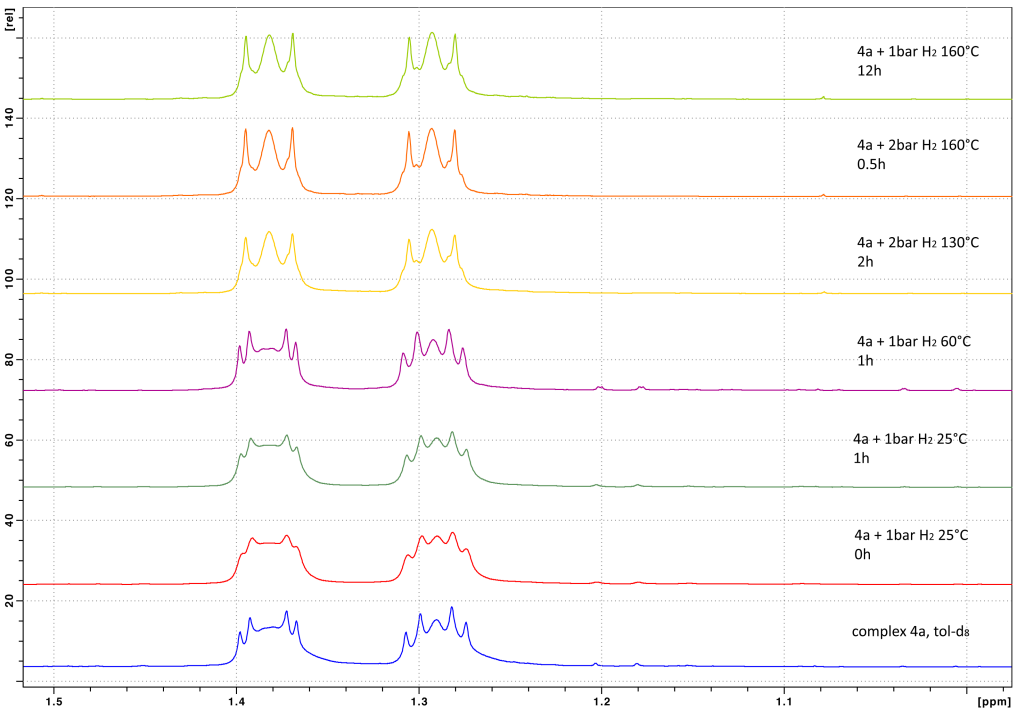

Figure S21: Section of stacked ^{1}H NMR spectra (500.13 MHz, toluene-d_8) of the P–(CH_3)$_3$ resonances of complex **4a** under variable H_2 pressure and temperature.

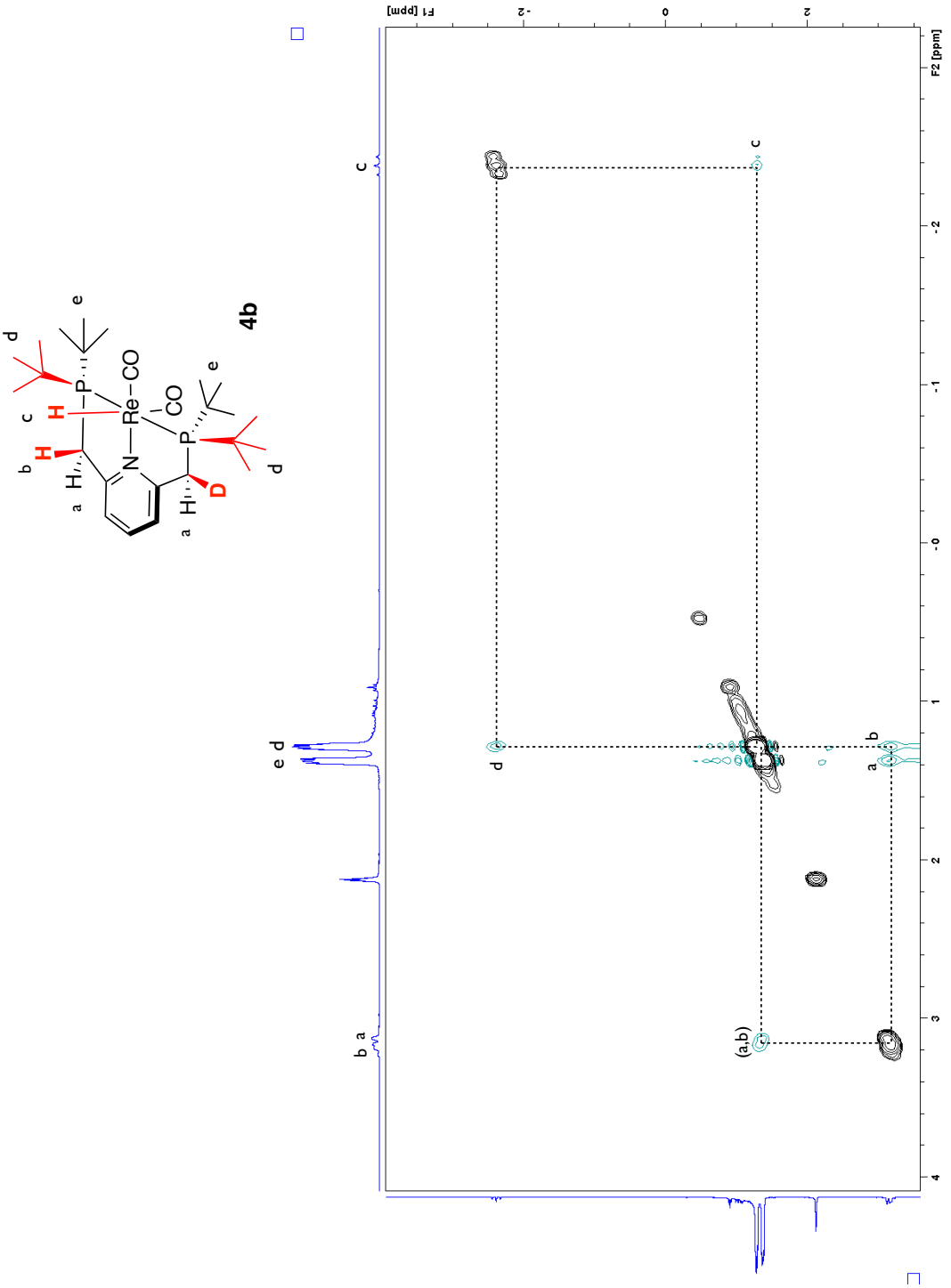

Figure S22: Section of the ^{1}H ^{1}H NOESY NMR spectrum (400 MHz, toluene-d_8) of complex **4b**.

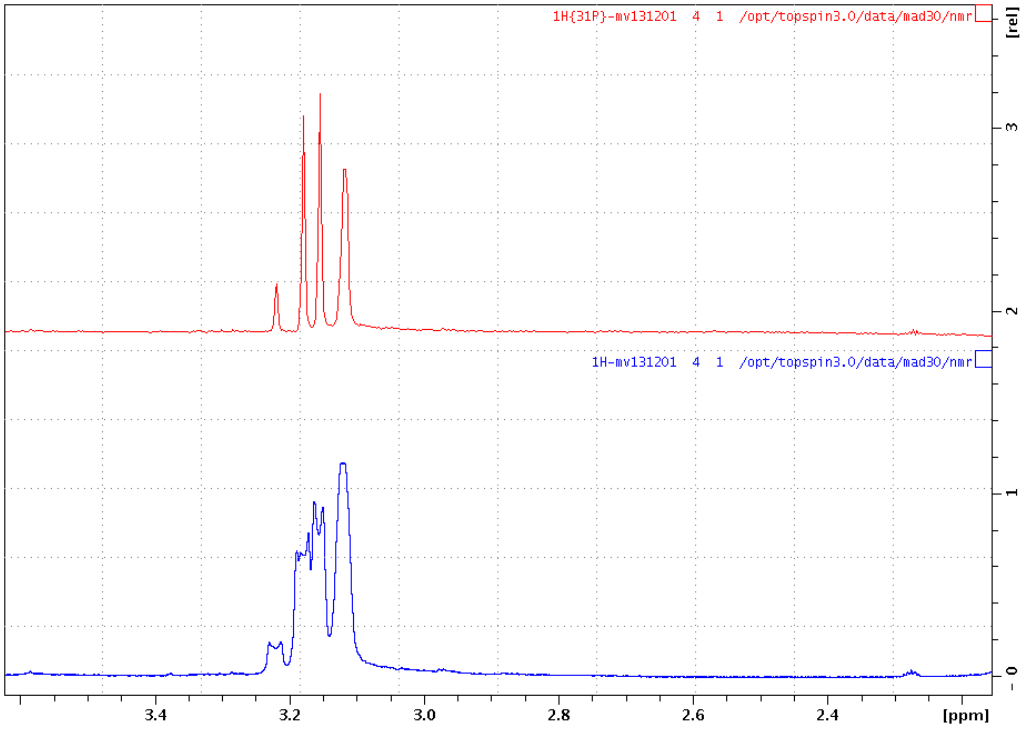

Figure S23: Section of the ^{1}H NMR spectrum of the *exo*-cyclic CH_2 moiety (bottom, blue) and $^{1}H\{^{31}P\}$ NMR spectrum (top, red) of complex **4a (**400 MHz, toluene-d_8).

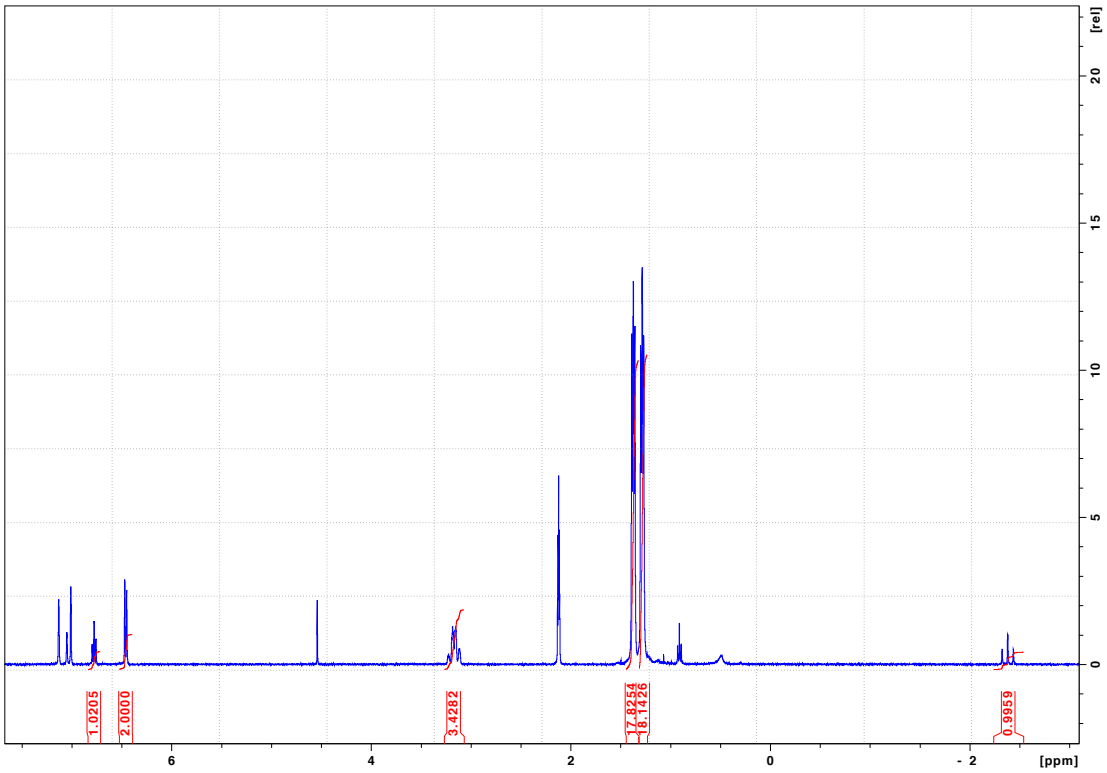

Figure S24: The ^{1}H NMR (400 MHz, toluene-d_8) spectrum of Complex **4b** (10 mg in 0.5 mL toluene-d_8) pressurized with 1 bar H_2 after heating at 100°C for 24h – Formation of **4** in 43% yield.

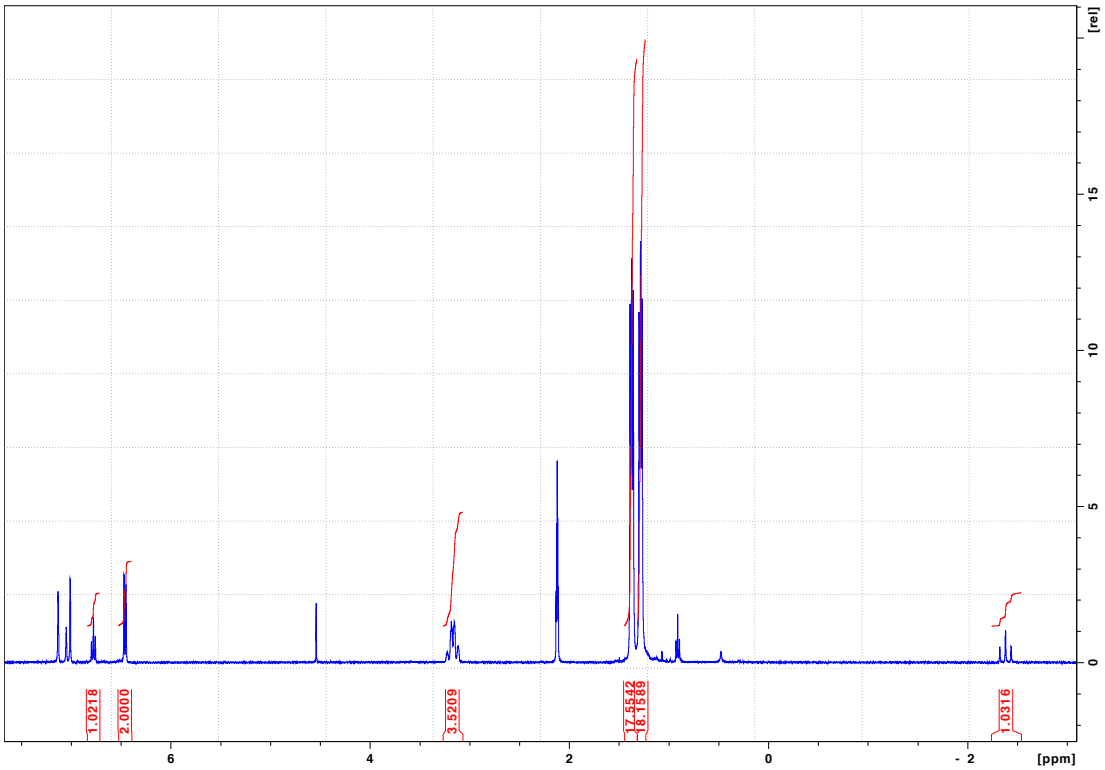

Figure S25: The ^{1}H NMR (400 MHz, toluene-d_8) spectrum of Complex **4b** (10 mg in 0.5 mL toluene-d_8) pressurized with 1 bar H_2 after heating at 100°C for 48h – Formation of **4** in 52% yield.

1.5. NMR spectra of [Re(PNP^{tBu})(CO)$_2$(OOCH)] (**5**).

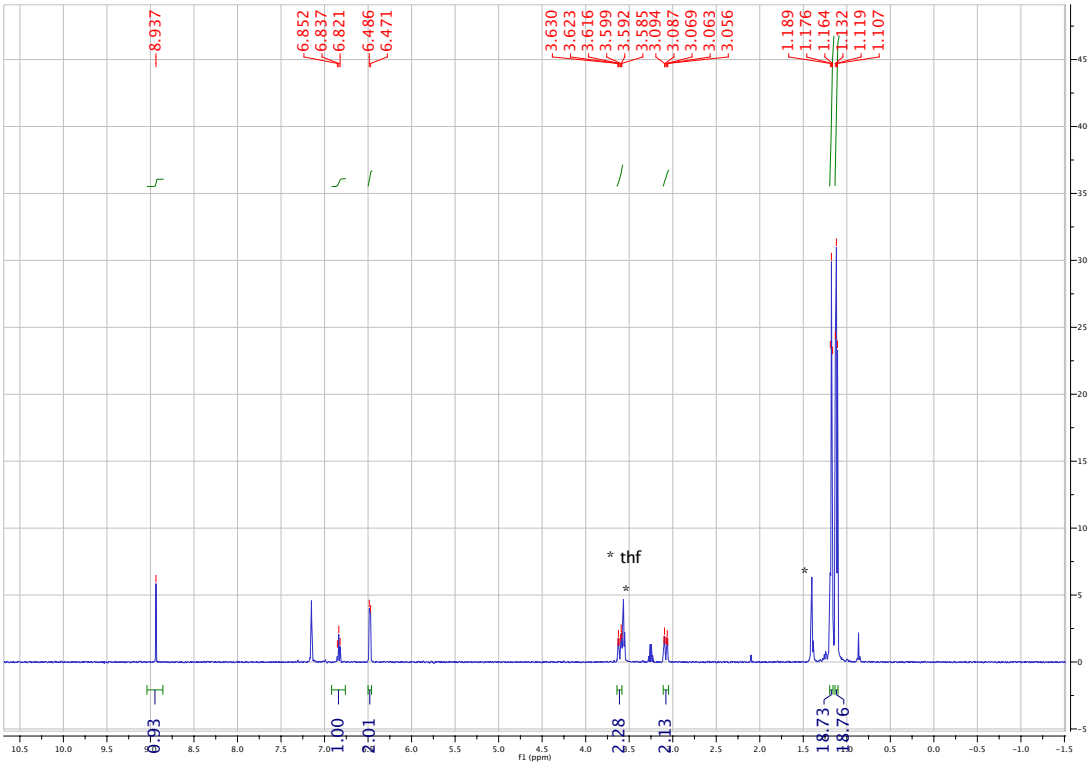

Figure S26: ^{1}H NMR spectrum (500.13 MHz C_6D_6, 25°C, sparsely soluble) of complex **5**.

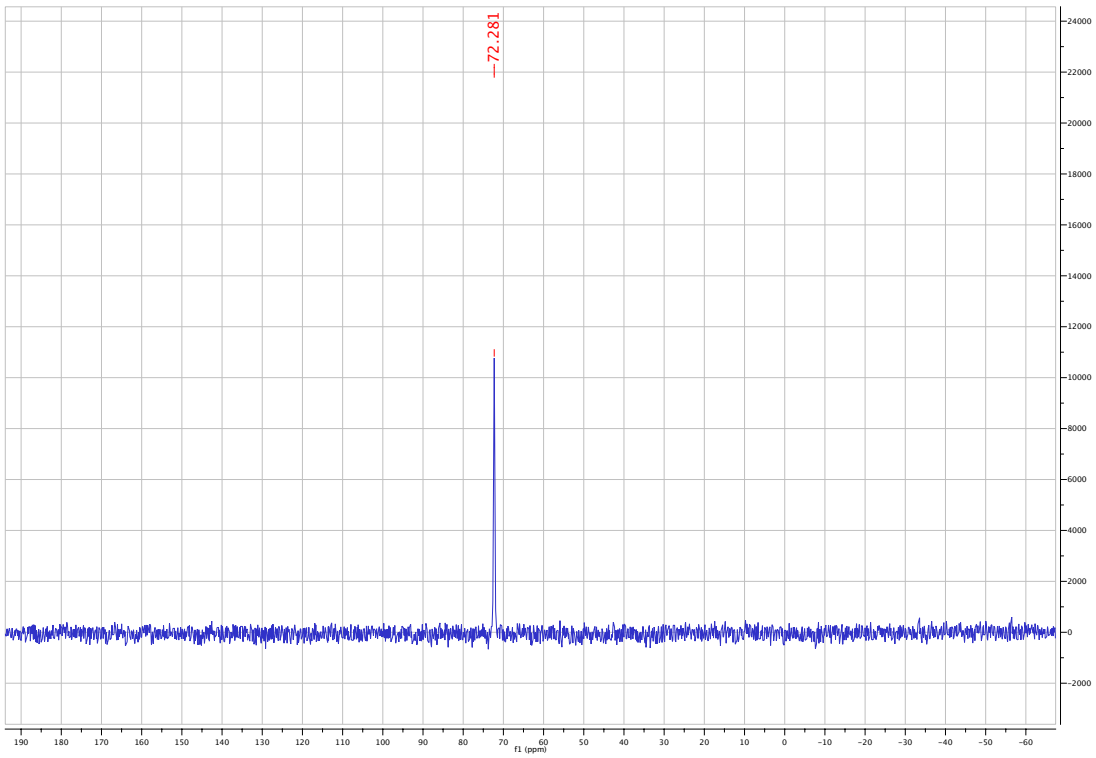

Figure S27: ^{31}P{^{1}H} NMR spectrum (202.5 MHz, C_6D_6, 25°C, sparsely soluble) of complex **5**.

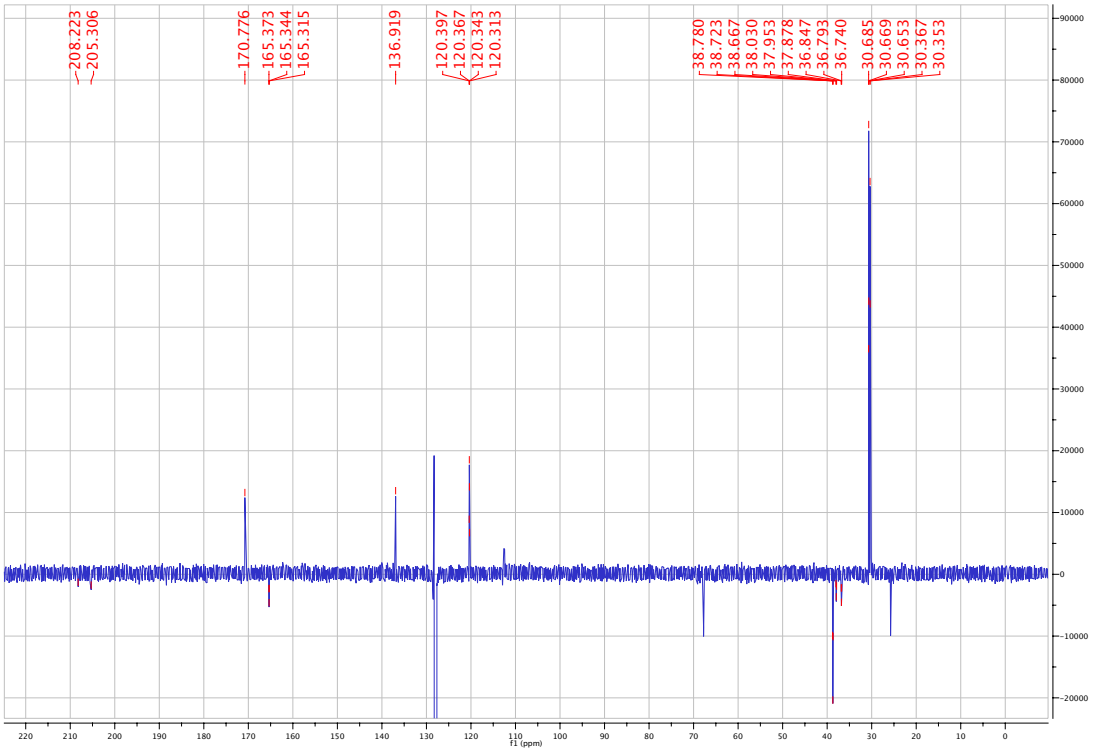

Figure S28: $^{13}C\{^{1}H\}$ QDEPT NMR spectrum (125.8 MHz, C_6D_6, 25°C, sparsely soluble) of complex **5**.