Supporting Information

Rhenium Carbyne and η^2-vinyl Complexes from One Pot Reactions of $ReH_5(PMe_2Ph)_3$ with Terminal Alkynes

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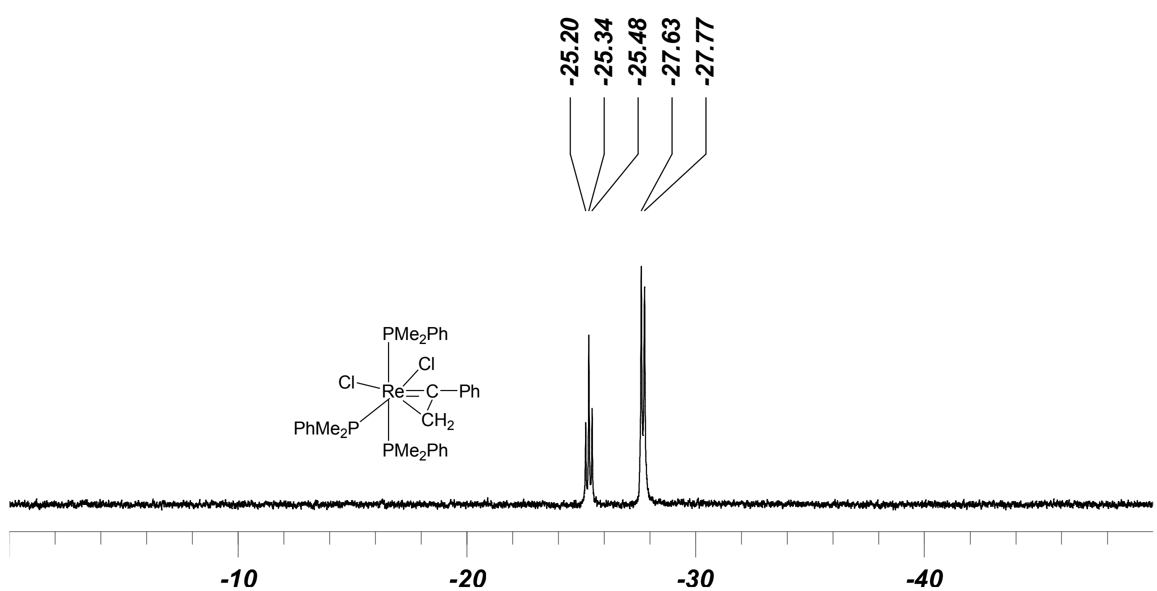

Figure S1. The $^{31}P\{^{1}H\}$ NMR spectrum of $Re(\eta^2\text{-}CH_2CPh)Cl_2(PMe_2Ph)_3$ (**3**) in $CDCl_3$.

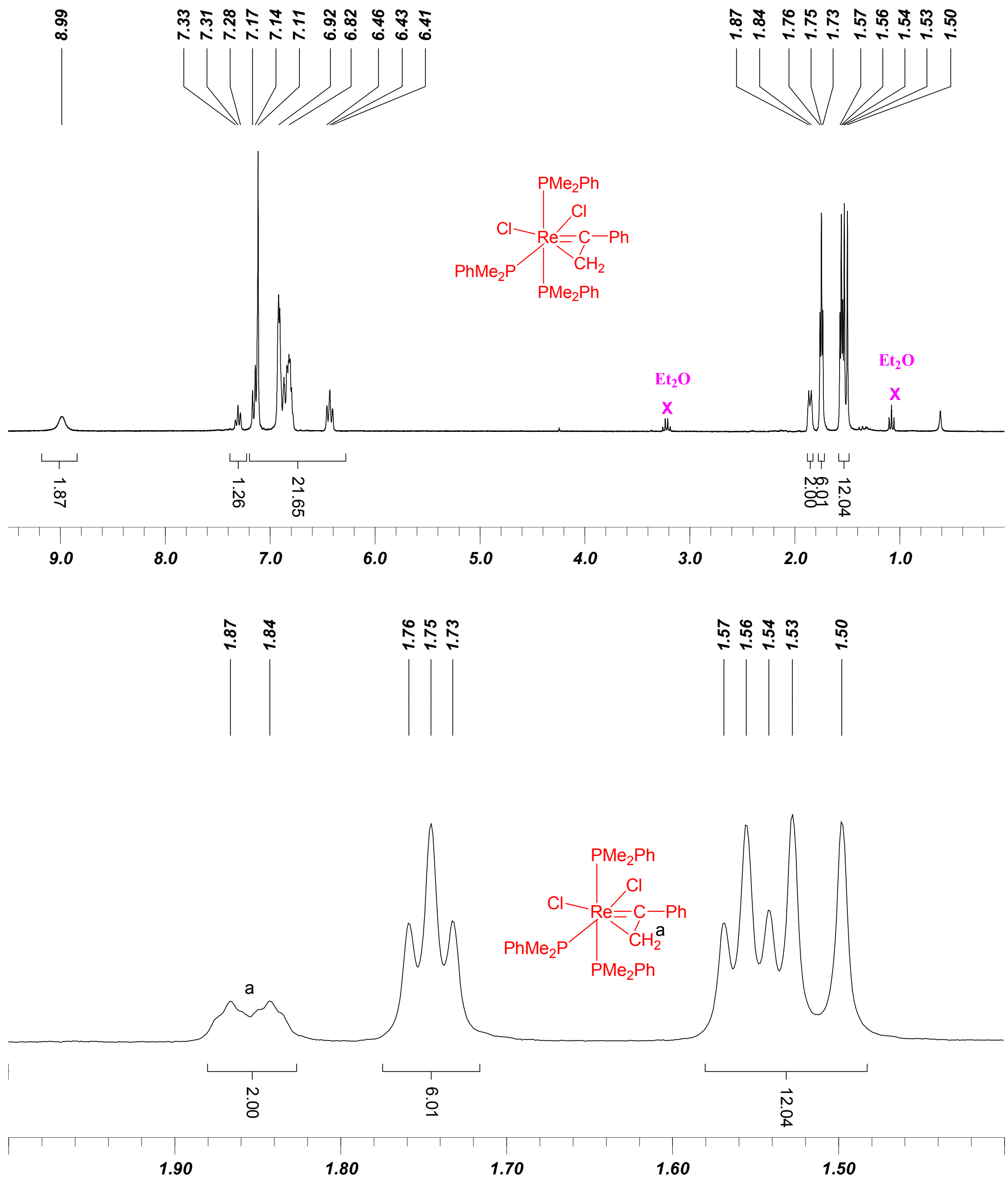

Figure S2. The ^{1}H NMR spectrum of Re(η^2-CH_2CPh)Cl_2(PMe_2Ph)$_3$ (**3**) in $CDCl_3$. Top, full spectrum; bottom, the expanded spectrum in the region of 1.4 -2 ppm.

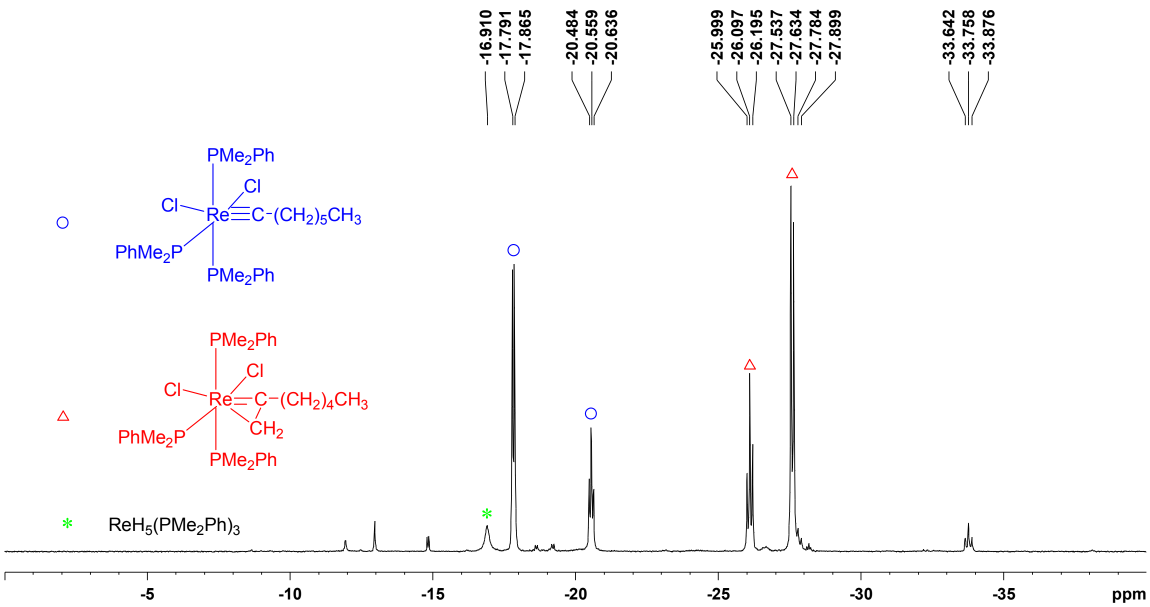

Figure S3. The $^{31}P\{^{1}H\}$ NMR spectrum of the crude product (in CD_2Cl_2) from the reaction of $ReH_5(PMe_2Ph)_3$ (0.859 g, 1.42 mmol) with 1-heptyne (0.178 g, 1.86 mmol) and hydrogen chloride (1.0 M in diethyl ether, 3.1 mL, 3.10 mmol). The $^{31}P\{^{1}H\}$ NMR data suggest that the major products of the reaction are $Re(\equiv C(CH_2)_5CH_3)Cl_2(PMe_2Ph)_3$ (**4**, o) and $Re(\eta^2\text{-}CH_2C(CH_2)_4CH_3)Cl_2(PMe_2Ph)_3$ (**5**, Δ). The minor peak at -16.9 ppm is due to un-reacted $ReH_5(PMe_2Ph)_3$ (*).

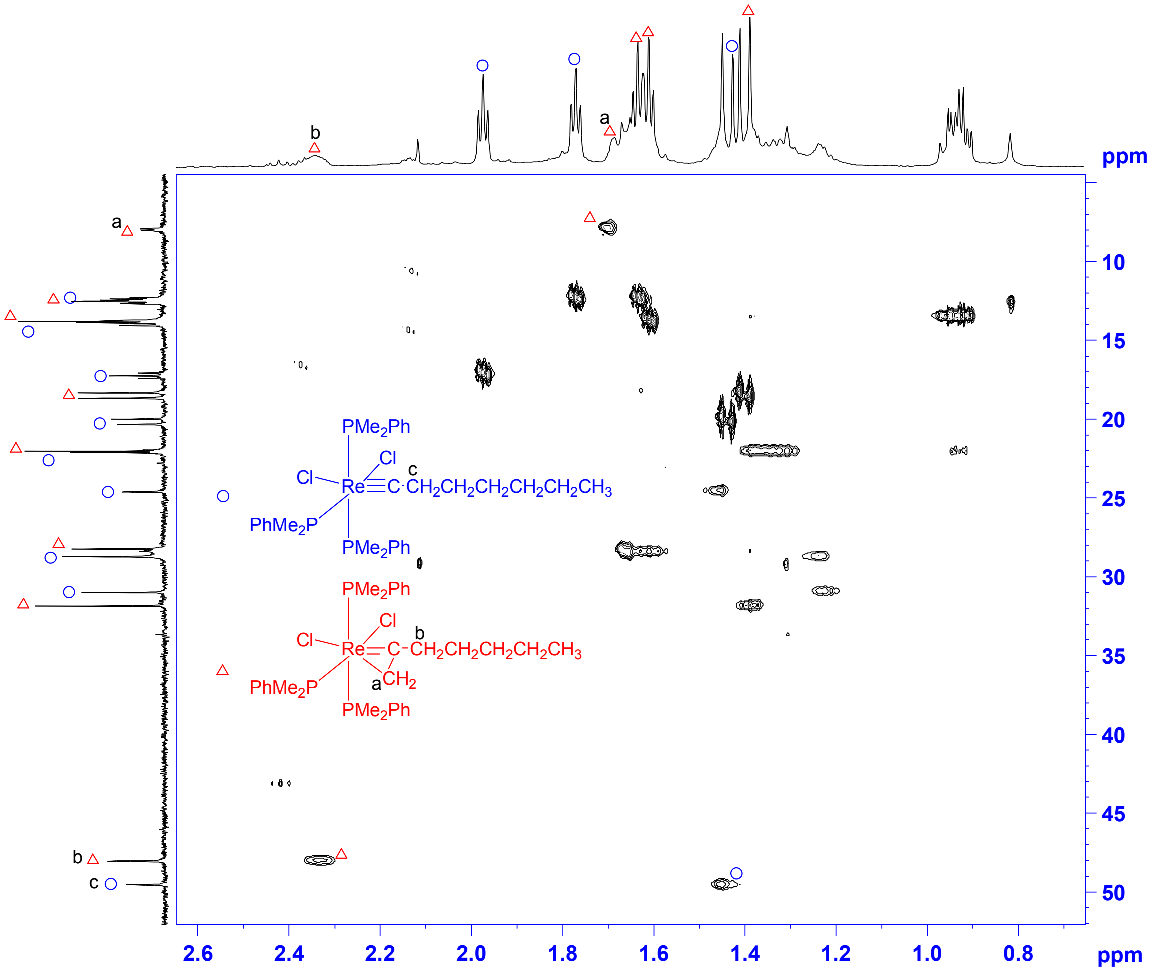

Figure S4. The expanded ^{1}H-^{13}C COSY spectrum (^{1}H, 0.6-2.7 ppm; ^{13}C, 5-52 ppm) of the crude product (in CD_2Cl_2) from the reaction of $ReH_5(PMe_2Ph)_3$ (0.859 g, 1.42 mmol) with 1-heptyne (0.178 g, 1.86 mmol) and hydrogen chloride (1.0 M in diethyl ether, 3.1 mL, 3.10 mmol). The NMR data confirm that the main products of the reaction are $Re(\equiv C(CH_2)_5CH_3)Cl_2(PMe_2Ph)_3$ (**4,** o) and $Re(\eta^2\text{-}CH_2C(CH_2)_4CH_3)Cl_2(PMe_2Ph)_3$ (**5,** Δ).

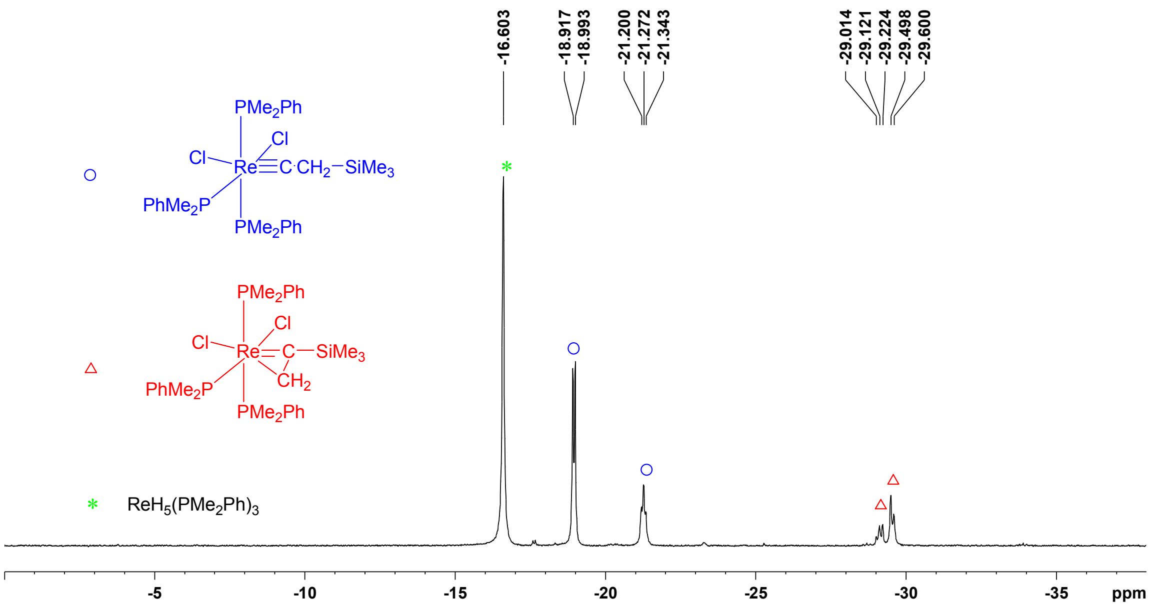

Figure S5. The *in situ* $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture produced from the reaction of $ReH_5(PMe_2Ph)_3$ (11.2 mg, 0.018 mmol) in benzene-d_6 (0.4 mL) with (trimethylsilyl)acetylene (3 µL, 0.021 mmol) and hydrogen chloride (0.050 mL, 0.05 mmol, 1.0 M in diethyl ether) for 4 h. The $^{31}P\{^{1}H\}$ NMR data suggest that the major products of the reaction are $Re(\equiv CCH_2SiMe_3)Cl_2(PMe_2Ph)_3$ (**6**, o) and $Re(\eta^2\text{-}CH_2CSiMe_3)Cl_2(PMe_2Ph)_3$ (**7**, Δ). The peak at -16.6 ppm is due to un-reacted $ReH_5(PMe_2Ph)_3$ (*).

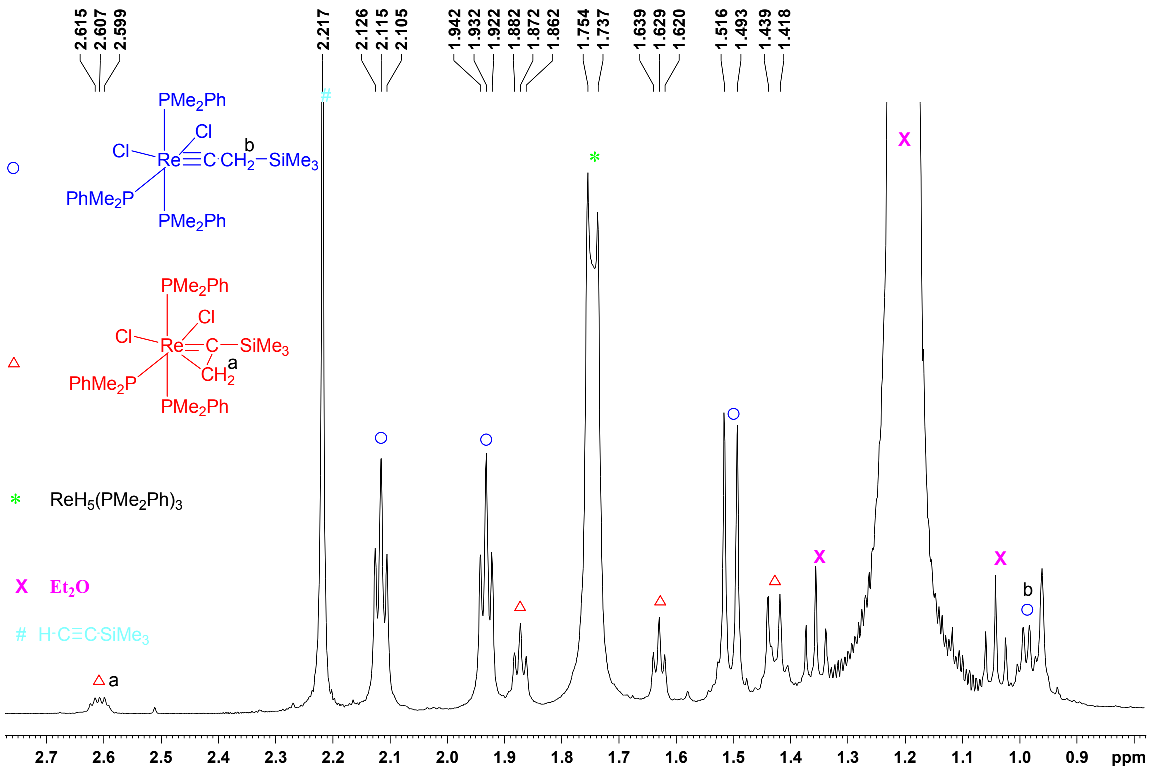

Figure S6. The expanded *in situ* ^{1}H NMR spectrum (in the region of 0.8 -2.8 ppm) of the reaction mixture produced from the reaction of $ReH_5(PMe_2Ph)_3$ (11.2 mg, 0.018 mmol) in benzene-d_6 (0.4 mL) with (trimethylsilyl)acetylene (3 µL, 0.021 mmol) and hydrogen chloride (0.050 mL, 0.05 mmol, 1.0 M in diethyl ether) for 4 h. The NMR data confirm that the major products of the reaction are $Re(\equiv CCH_2SiMe_3)Cl_2(PMe_2Ph)_3$ (**6**, o) and $Re(\eta^2-CH_2CSiMe_3)Cl_2(PMe_2Ph)_3$ (**7**, Δ).

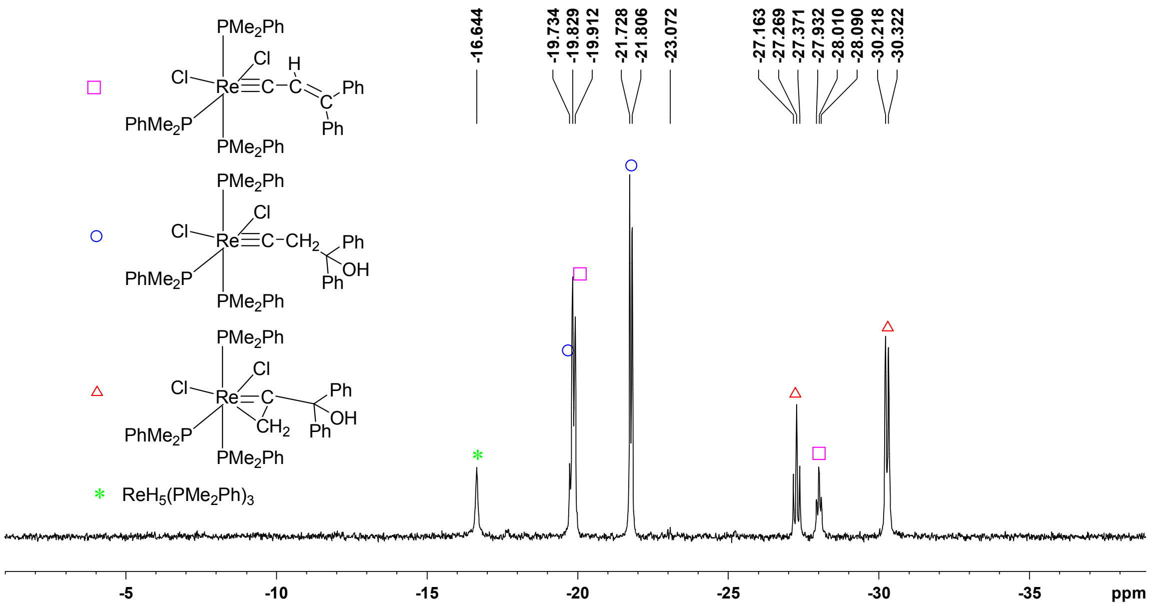

Figure S7. The *in situ* $^{31}P\{^1H\}$ NMR spectra of the reaction mixture produced from the reaction of $ReH_5(PMe_2Ph)_3$ (27 mg, 0.044 mmol) with 1,1-diphenyl-2-propyn-1-ol (10.1 mg, 0.048 mmol) in benzene-d_6 (0.4 mL) and hydrogen chloride (1.0 M in diethyl ether, 90 µL, 0.09 mmol) for 24 h. The $^{31}P\{^1H\}$ NMR data suggest that the major products of the reaction are Re(≡CCH=CPh_2) $(PMe_2Ph)_3$ (**8**, □), Re(≡$CCH_2C(OH)Ph_2$)$Cl_2(PMe_2Ph)_3$ (**9**, o) and Re(η^2-$CH_2CC(OH)Ph_2$)$Cl_2(PMe_2Ph)_3$ (**10,** Δ). The peak at -16.6 ppm is due to un-reacted $ReH_5(PMe_2Ph)_3$ (*).

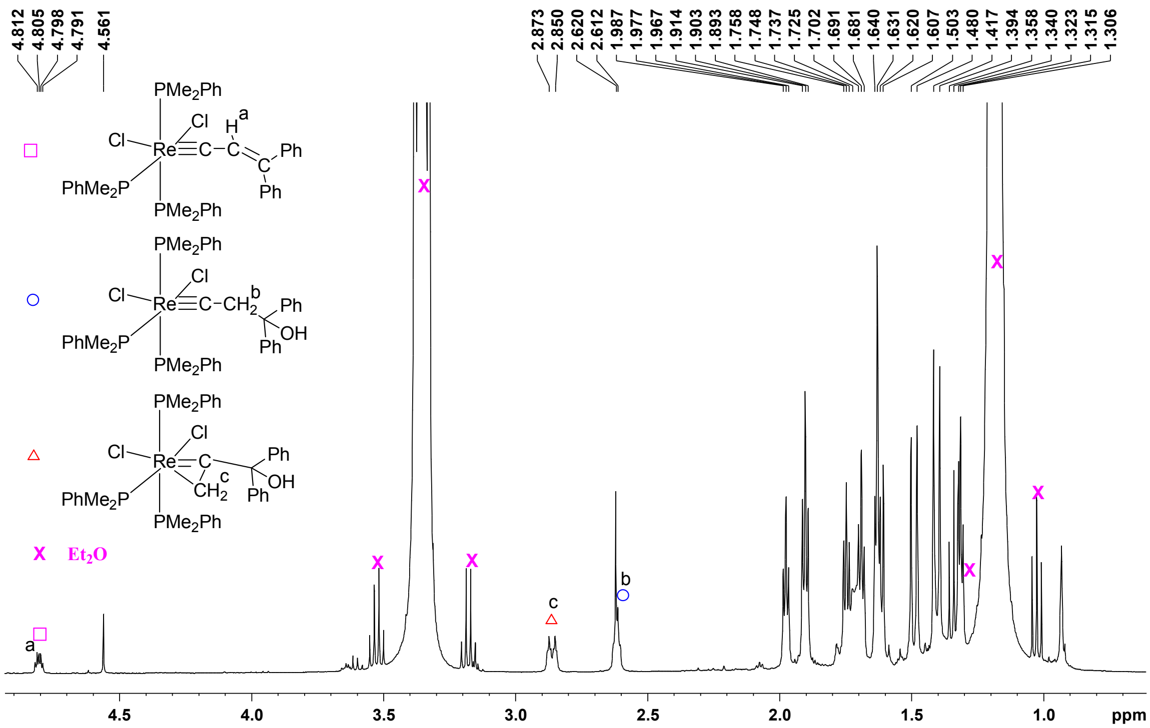

Figure S8. The expanded *in situ* ^{1}H NMR spectrum (in the region of 0 – 5 ppm) of the reaction mixture produced from the reaction of $ReH_5(PMe_2Ph)_3$ (27 mg, 0.044 mmol) with 1,1-diphenyl-2-propyn-1-ol (10.1 mg, 0.048 mmol) in benzene-d_6 (0.4 mL) and hydrogen chloride (1.0 M in diethyl ether, 90 μL, 0.09 mmol) for 24 h. The NMR data confirms that the reaction produced $Re(\equiv CCH{=}CPh_2)$ $(PMe_2Ph)_3$ (**8**, □), $Re(\equiv CCH_2C(OH)Ph_2)Cl_2(PMe_2Ph)_3$ (**9**, o) and $Re(\eta^2\text{-}CH_2{=}CC(OH)Ph_2)Cl_2(PMe_2Ph)_3$ (**10**, Δ).