Electronic Supporting Information

pKa of Alcohols Dictate their Reactivity with Reduced Uranium-substituted Thiomolybdate Clusters

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Supporting Information Table of Contents

Table S1: Crystallographic parameters for molecular structures of complexes for **$(Cp^*_3Mo_3S_4)Cp^*U(OMe)$**, **$(Cp^*_3Mo_3S_4)Cp^*U(OPh^{Cl2})$**, **$(Cp^*_3Mo_3S_4)Cp^*U(OPh)_2$** and **$(Cp^*_3Mo_3S_4)U(O^tBu)_3$.**

Compound	**$(Cp^*_3Mo_3S_4)Cp^*U(OMe)$**	**$(Cp^*_3Mo_3S_4)Cp^*U(OPh^{Cl2})$**	**$(Cp^*_3Mo_3S_4)Cp^*U(OPh)_2$**	**$(Cp^*_3Mo_3S_4)U(O^tBu)_3$**
Empirical formula	$C_{41}H_{63}Mo_3OS_4U$	$C_{56.50}H_{75}Cl_2Mo_3O\ S_4U$	$C_{58}H_{70}D_6Mo_3O_2S_4U$	$C_{42}H_{72}Mo_3O_3S_4U$
Formula weight	1226.00	1495.15	1465.31	1279.08
Temperature	100.00(10) K	100.00(10) K	100.00(10) K	100.00(10) K
Wavelength	1.54184 Å	1.54184 Å	1.54184 Å	1.54184 Å
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	*$P2_1/n$*	*$P2_1/c$*	*$P2_12_12_1$*	*$P2_1/n$*
Unit cell dimensions	*a = 11.17593(8) Å* *b = 19.26021(16) Å* *c = 20.25129(16)* *α = 90°* *β = 99.7002(7)°* *Å γ = 90°*	*a = 11.11244(9) Å* *b = 20.41551(16) Å* *c = 24.6678(2) Å* *α = 90°* *γ = 90°* *β = 97.3244(8)°*	*a = 10.99181(6) Å* *b = 20.28569(11) Å* *c = 24.73170(15) Å* *α = 90°* *β = 90°* *γ = 90°*	*a = 10.97728(7) Å* *b = 17.85746(11) Å* *c = 24.61165(16) Å* *α = 90°* *β = 96.2794(6)°* *γ = 90°*
Volume / Å^3	4296.78(6)	5550.63(8)	5514.59(5)	4795.59(5)
Z	4	4	4	4
Crystal Size	0.103 x 0.053 x 0.027 mm^3	0.169 x 0.028 x 0.019 mm^3	0.138 x 0.038 x 0.015 mm^3	0.127 x 0.065 x 0.011 mm^3
Reflections collected	62579	92991	63887	80766
Independent reflections	9171 [*R*(int) = 0.0510]	11963 [R(int) = 0.0516]	11807 [R(int) = 0.0481]	10319 [*R*(int) = 0.0533]
Completeness (θ = 74.5^o)	99.7%	99.9%	99.9%	99.9%
Goodness-of-fit on F^2	1.042	1.052	1.057	1.025
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.0457, *wR*2 = 0.1110	R1 = 0.0286, wR2 = 0.0704	R1 = 0.0249, wR2 = 0.0541	R1 = 0.0249, wR2 = 0.0581
Largest diff. peak and hole	3.004 and -3.149 e.Å^{-3}	4.102 and -2.074 e.Å^{-3}	1.454 and -0.874 e.Å^{-3}	1.219 and -1.055 e.Å^{-3}

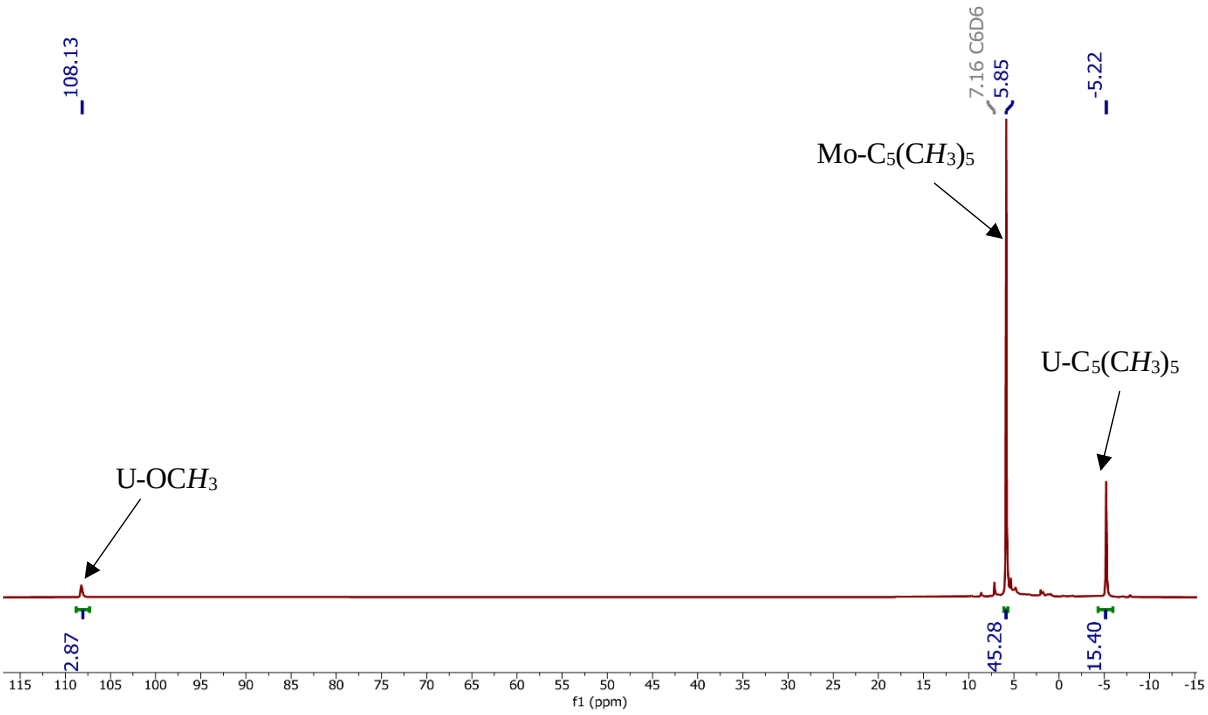

Figure S1. ^{1}H NMR spectrum (400 MHz) of ($Cp^{*}_{3}Mo_{3}S_{4}$)Cp*U(OMe) in $C_{6}D_{6}$.

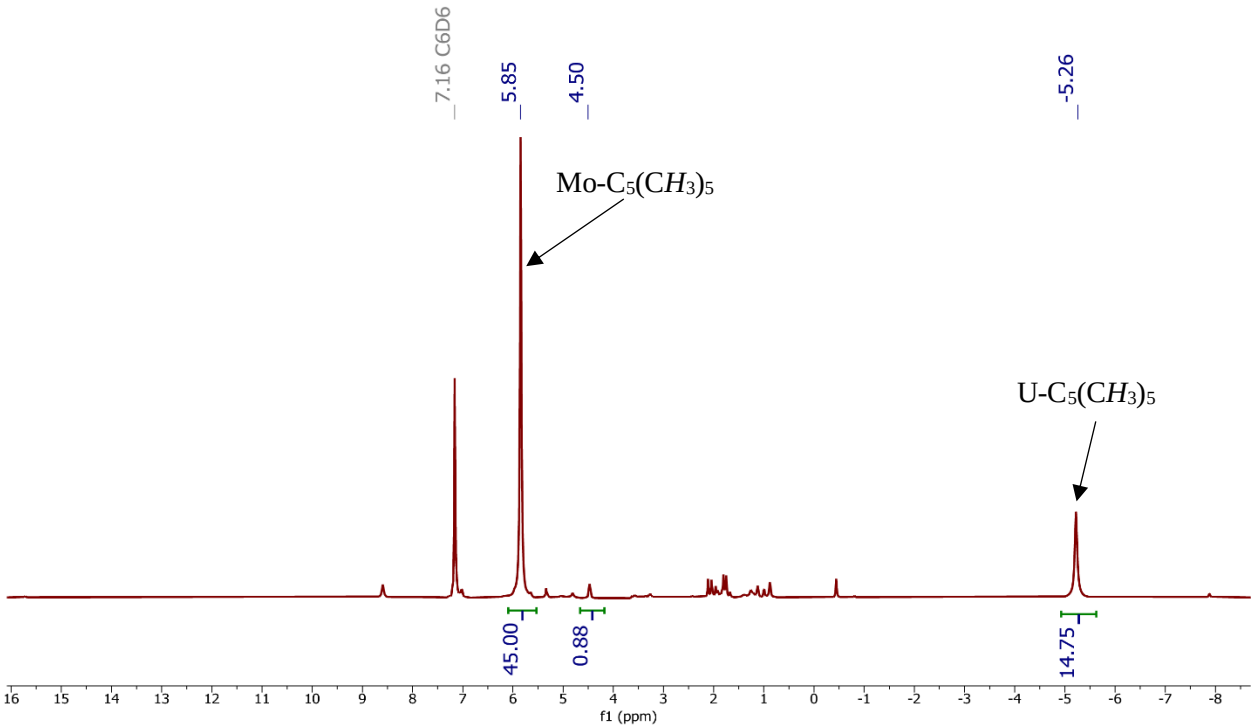

Figure S2. ^{1}H NMR spectrum (400 MHz) of ($Cp^{*}_{3}Mo_{3}S_{4}$)UCp* and $C_{6}D_{6}$ solution having 1 equivalent of methanol in $C_{6}D_{6}$. [Signals δ = 4.50 ppm is assigned to H_{2} (~88% yield).

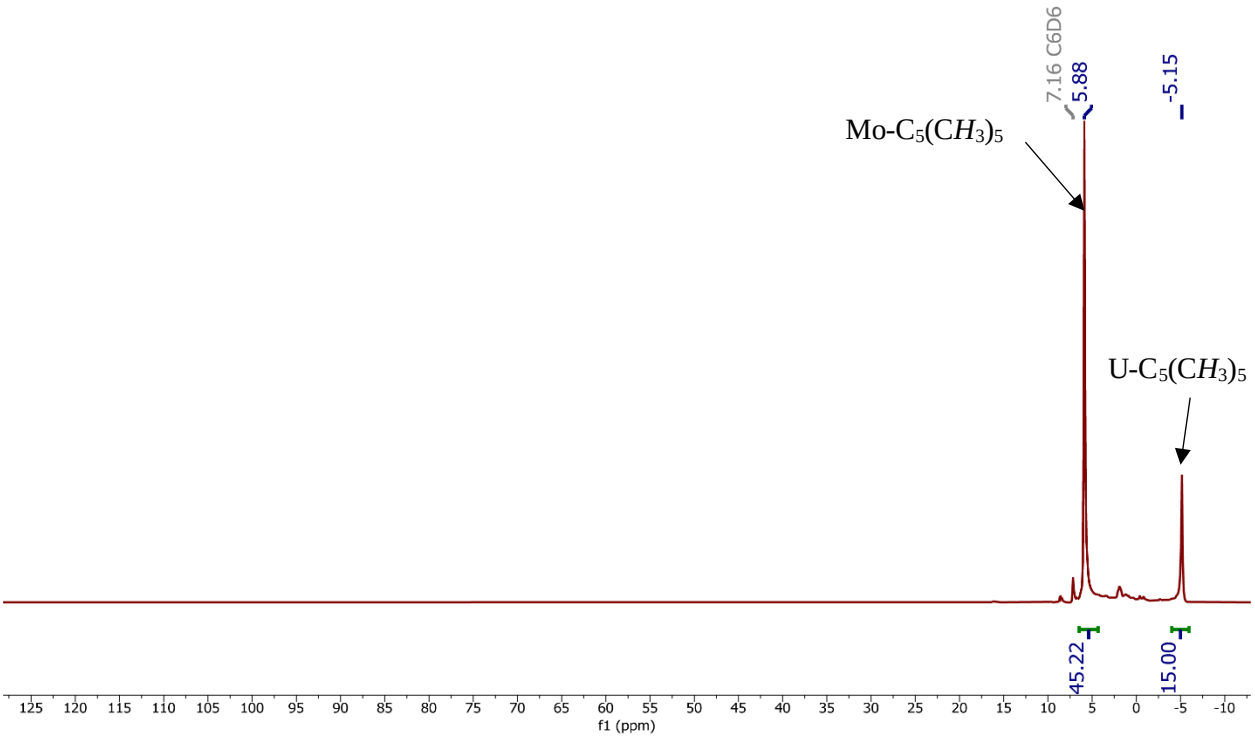

Figure S3. ^{1}H NMR spectrum (400 MHz) of ($Cp^{*}_{3}Mo_{3}S_{4}$)$Cp^{*}U(OCD_{3})$ in $C_{6}D_{6}$.

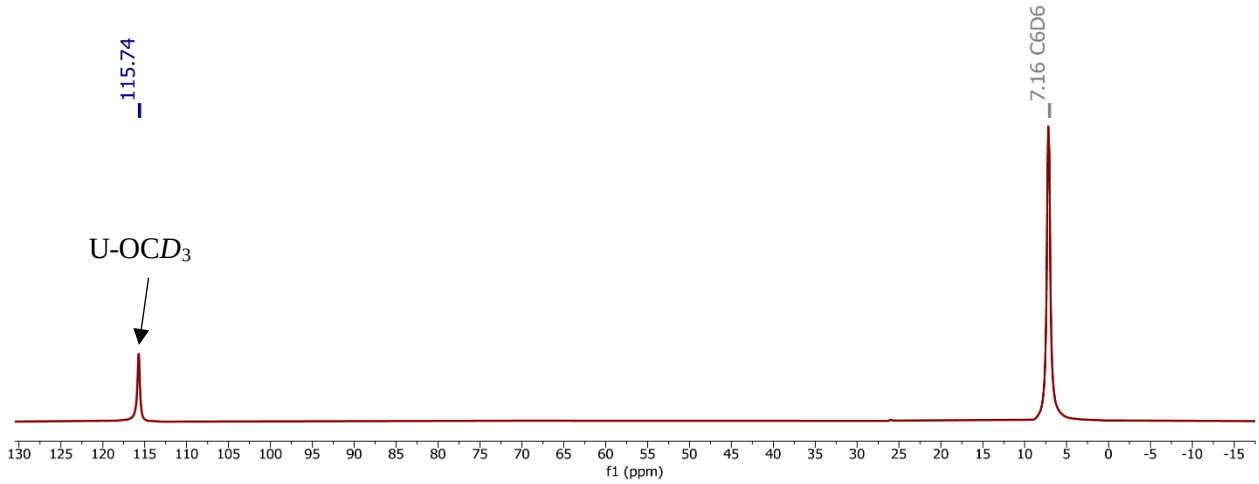

Figure S4. ^{2}H NMR spectrum (400 MHz) of ($Cp^{*}_{3}Mo_{3}S_{4}$)$Cp^{*}U(OCD_{3})$ in $C_{6}H_{6}$ [The signal at 115.74 ppm is attributed to the –O*C*D_{3}].

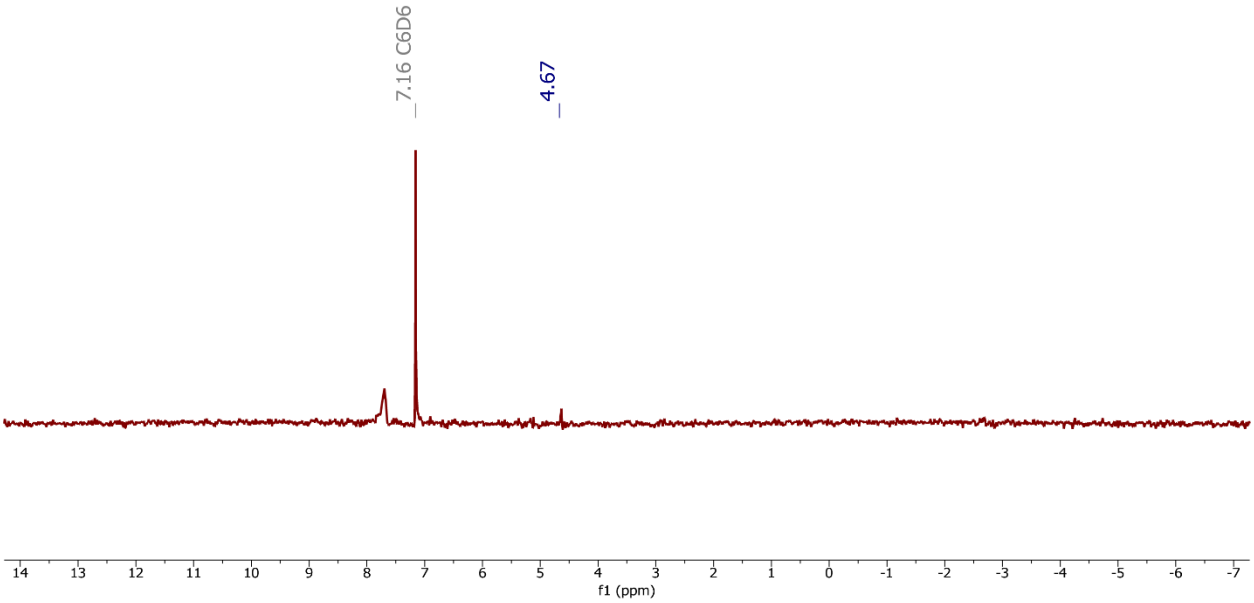

Figure S5. ^{2}H NMR spectrum (400 MHz) of the reaction mixture containing a C_6H_6 solution of $(Cp^*_3Mo_3S_4)UCp^*$ and a C_6H_6 solution with slightly more than 1 equivalent of CD_3OD [C_6D_6 was added as an internal reference; $\delta = 4.67$ ppm is assigned to D_2].

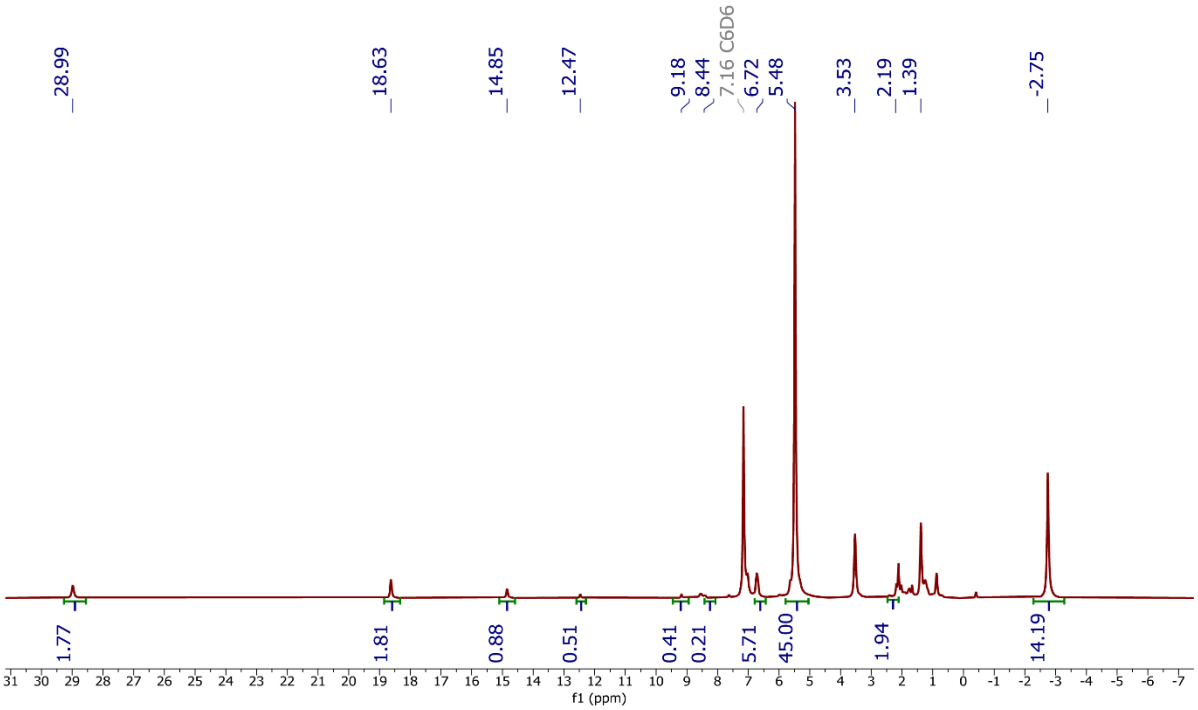

Figure S6. ^{1}H NMR spectrum (400 MHz) of the reaction mixture containing $(Cp^*_3Mo_3S_4)UCp^*$ and ~1.1 equivalent of phenol in C_6D_6. Signals at 28.99, 18.63, 14.85, 5.48 and -2.75 ppm correspond to $(Cp^*_3Mo_3S_4)Cp^*U(OPh)$, whereas signals at 12.47, 9.18, 8.44, 6.72 and 2.19 ppm correspond to $(Cp^*_3Mo_3S_4)Cp^*U(OPh)_2$.

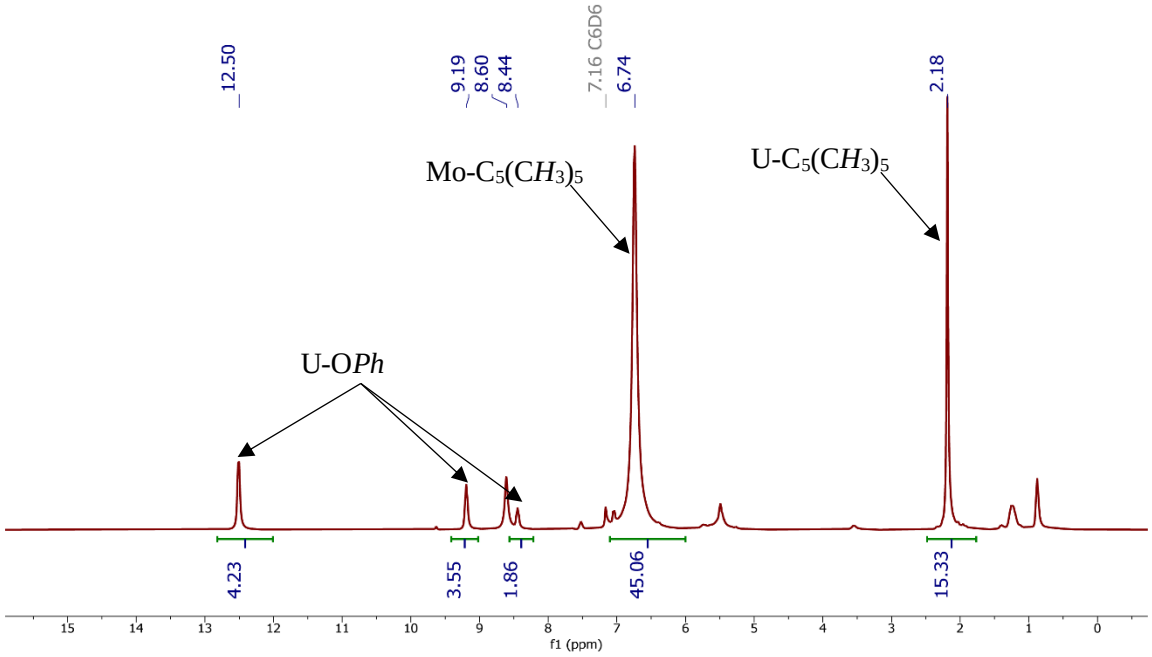

Figure S7. ^{1}H NMR spectrum (400 MHz) of $(Cp^{*}_{3}Mo_{3}S_{4})Cp^{*}U(OPh)_{2}$ in $C_{6}D_{6}$.

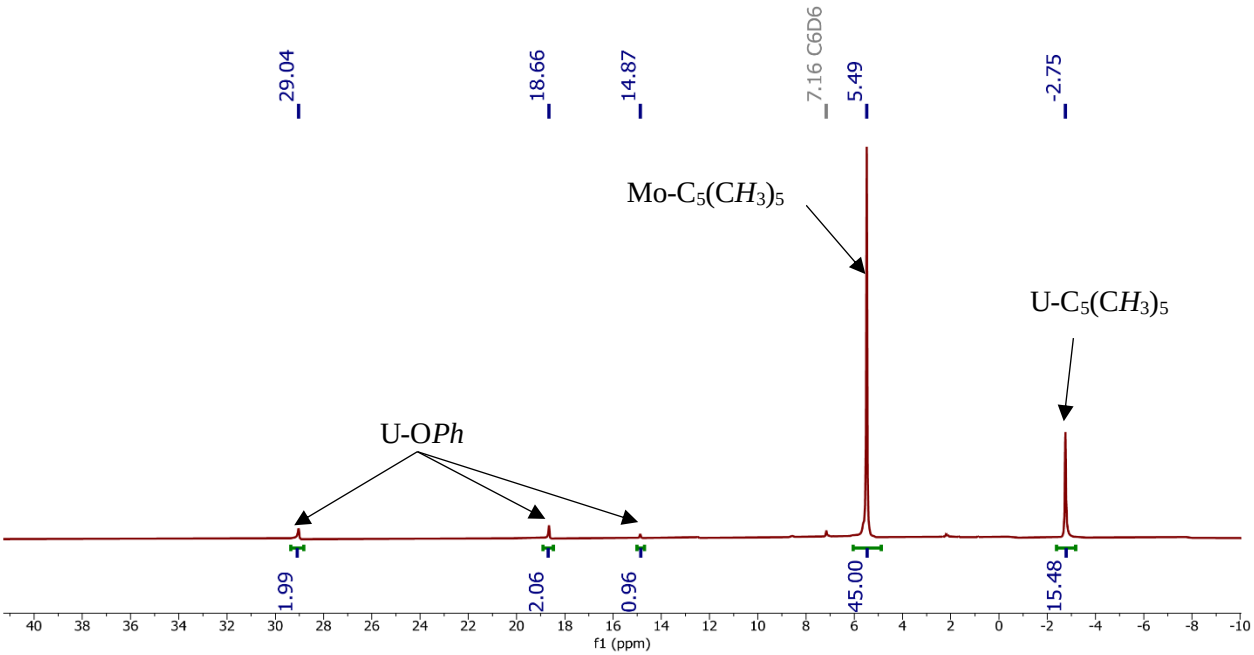

Figure S8. ^{1}H NMR spectrum (400 MHz) of $(Cp^{*}_{3}Mo_{3}S_{4})Cp^{*}U(OPh)$ in $C_{6}D_{6}$.

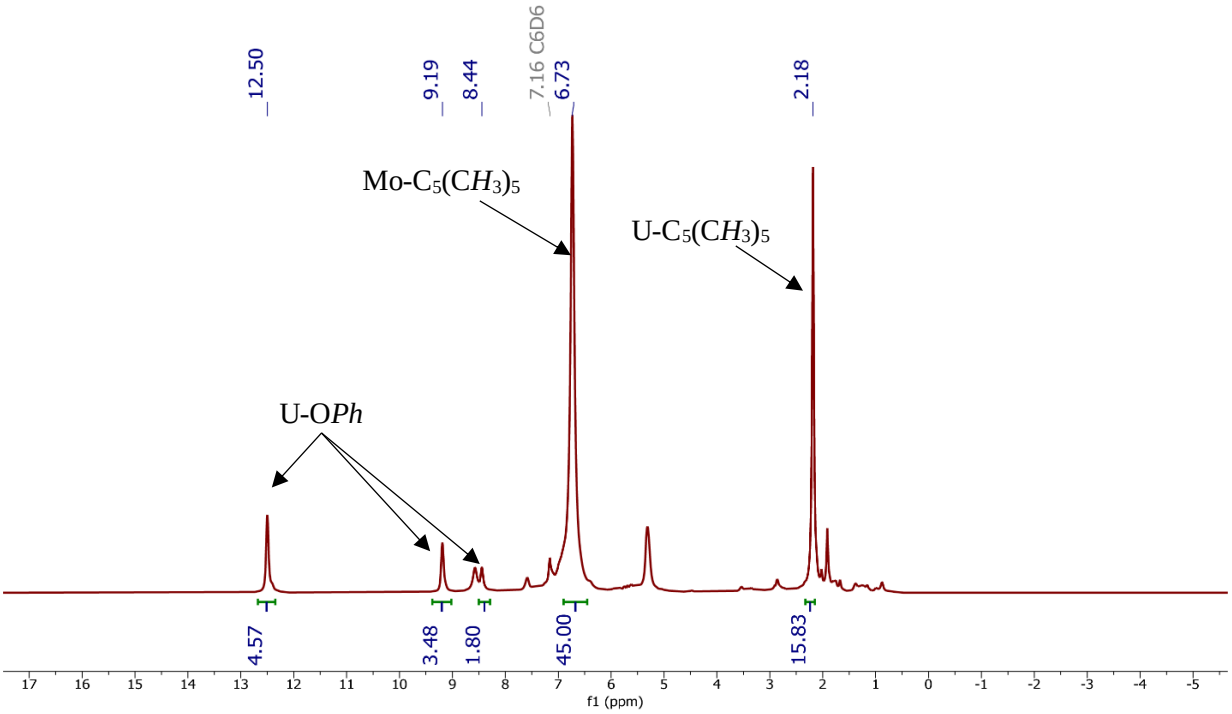

Figure S9. ^{1}H NMR spectrum (400 MHz) of $(Cp^*_3Mo_3S_4)Cp^*U(OPh)_2$ obtained from the reaction of $(Cp^*_3Mo_3S_4)Cp^*U(OPh)$ with 1 equivalent of phenol in C_6D_6.

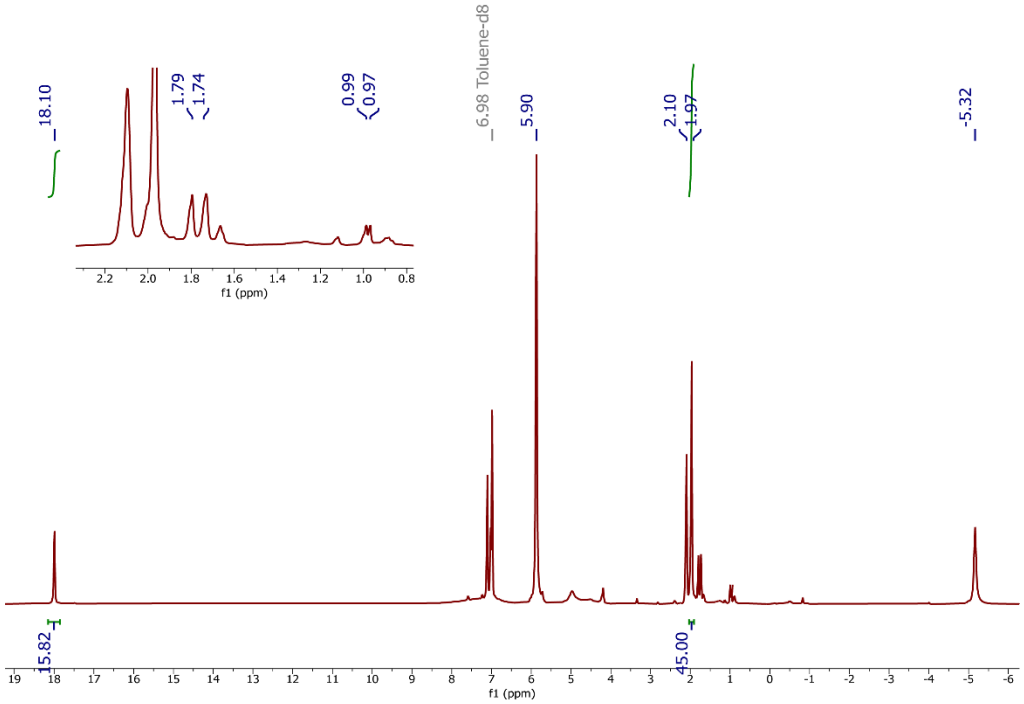

Figure S10. ^{1}H NMR spectrum (400 MHz) (with slow relaxation time) of the reaction mixture containing $(Cp^*_3Mo_3S_4)UCp^*$ and 2 equivalents methanol. (The signals at 18.10 and 1.97 ppm are assigned to $[(Cp^*_3Mo_3S_4)^+U(OMe)_5^-]$ or $[(Cp^*_3Mo_3S_4)U(OMe)_5]$; signals at 5.90 and -5.32 correspond to $[(Cp^*_3Mo_3S_4)Cp^*U(OMe)]$; and signals at 0.98, 1.72 and 1.79 ppm assigned to Cp*H.

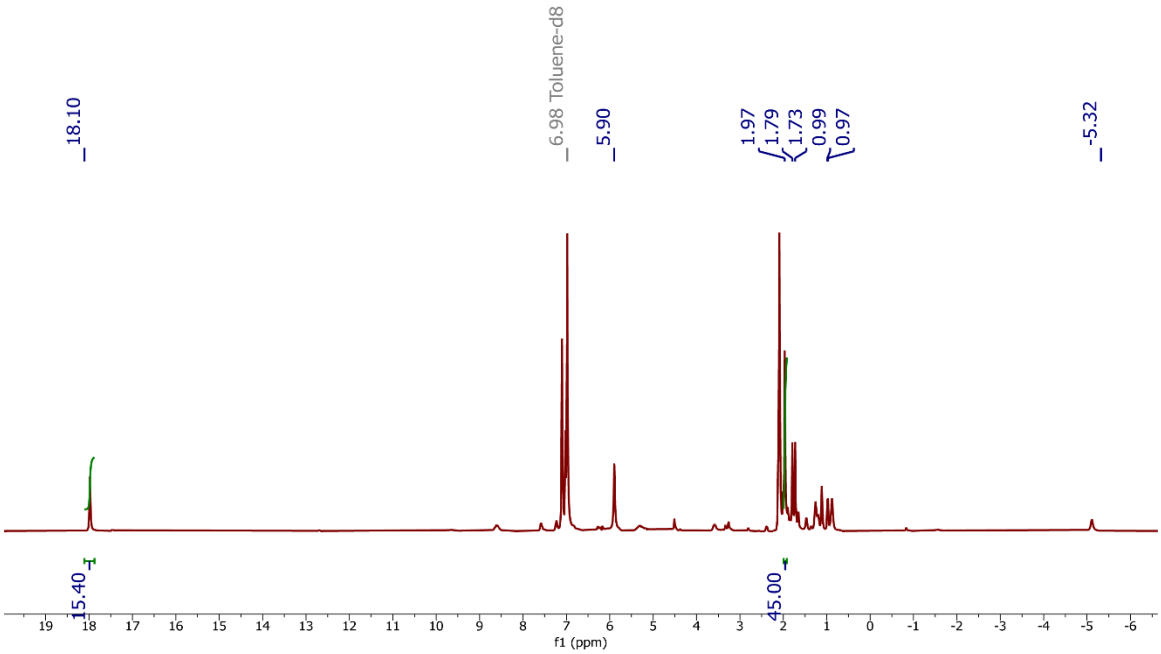

Figure S11. ^{1}H NMR spectrum (400 MHz) of the reaction mixture containing ($Cp^{*}_{3}Mo_{3}S_{4}$)UCp^{*} and 3 equivalents methanol.

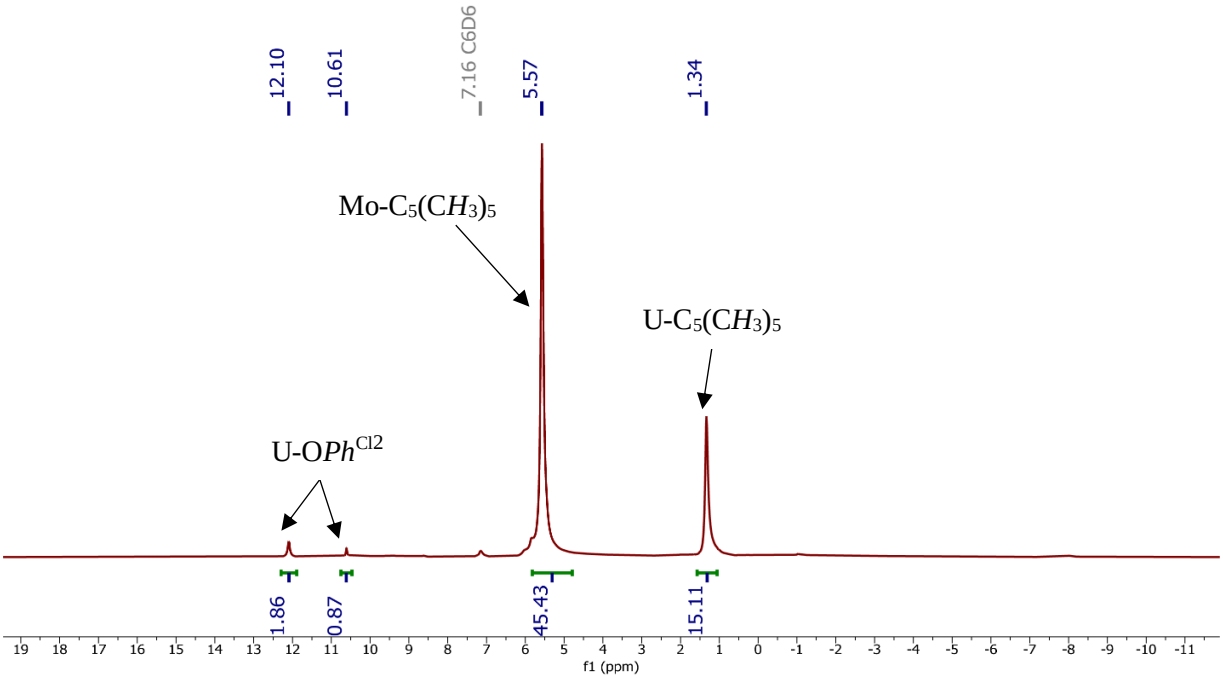

Figure S12. ^{1}H NMR spectrum (400 MHz) of ($Cp^{*}_{3}Mo_{3}S_{4}$)Cp^{*}U(OPh^{Cl2}) in $C_{6}D_{6}$.

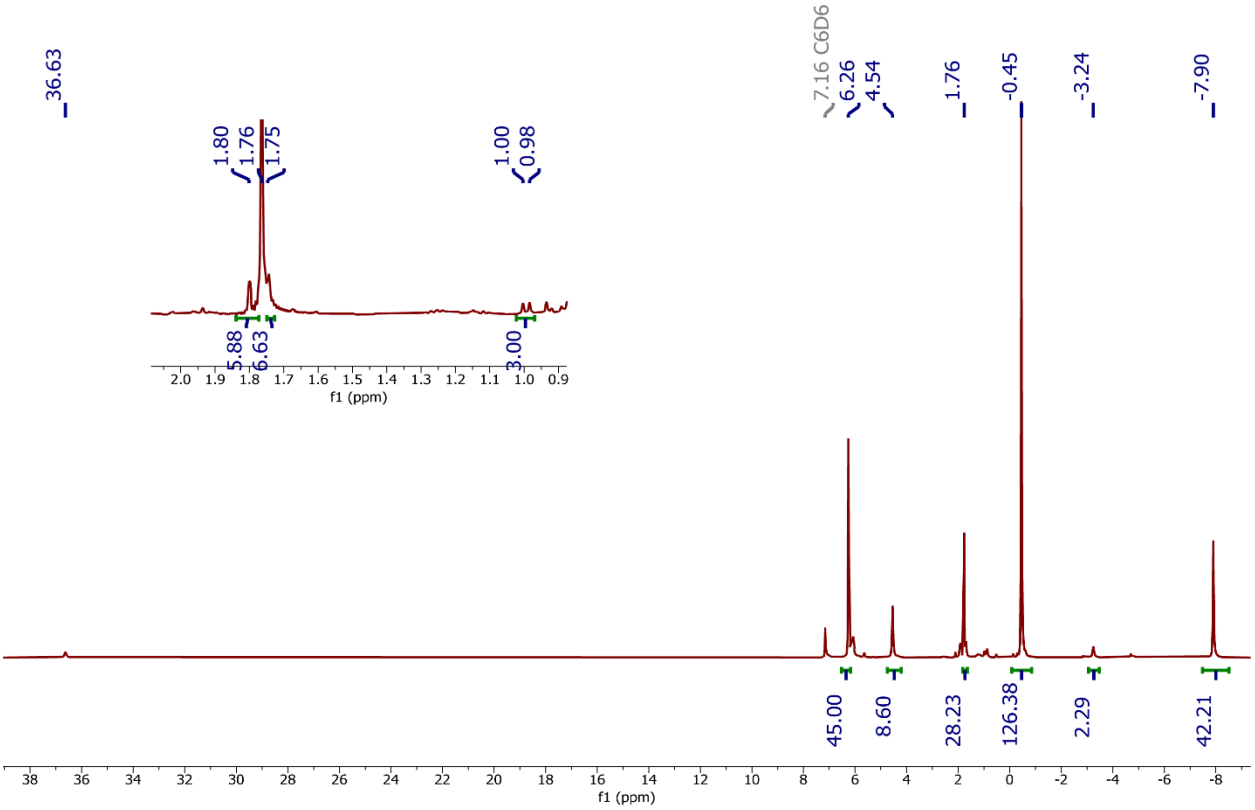

Figure S13. ^{1}H NMR spectrum (400 MHz) (with slow relaxation time) of the reaction mixture containing ($Cp^*_3Mo_3S_4$)UCp^* and 1 equivalent of *tert*-butanol in C_6D_6. The signals at 6.26, and 1.76 ppm correspond to ($Cp^*_3Mo_3S_4$)U(O^tBu)$_3$; signals at 4.54, -3.24, and 36.63 ppm correspond to proposed ($Cp^*_3Mo_3S_4$)Cp^*U(O^tBu) (($Cp^*_3Mo_3S_4$)U(O^tBu)$_3$: ($Cp^*_3Mo_3S_4$)Cp^*U(O^tBu) ~ 5:1) (see figure S20 for the ^{1}H NMR spectrum of pure ($Cp^*_3Mo_3S_4$)Cp^*U(O^tBu)); signals at 1.80, 1.75, and 0.99 ppm correspond Cp^*H; signals at -0.45 and -7.90 ppm correspond to ($Cp^*_3Mo_3S_4$)UCp^*.

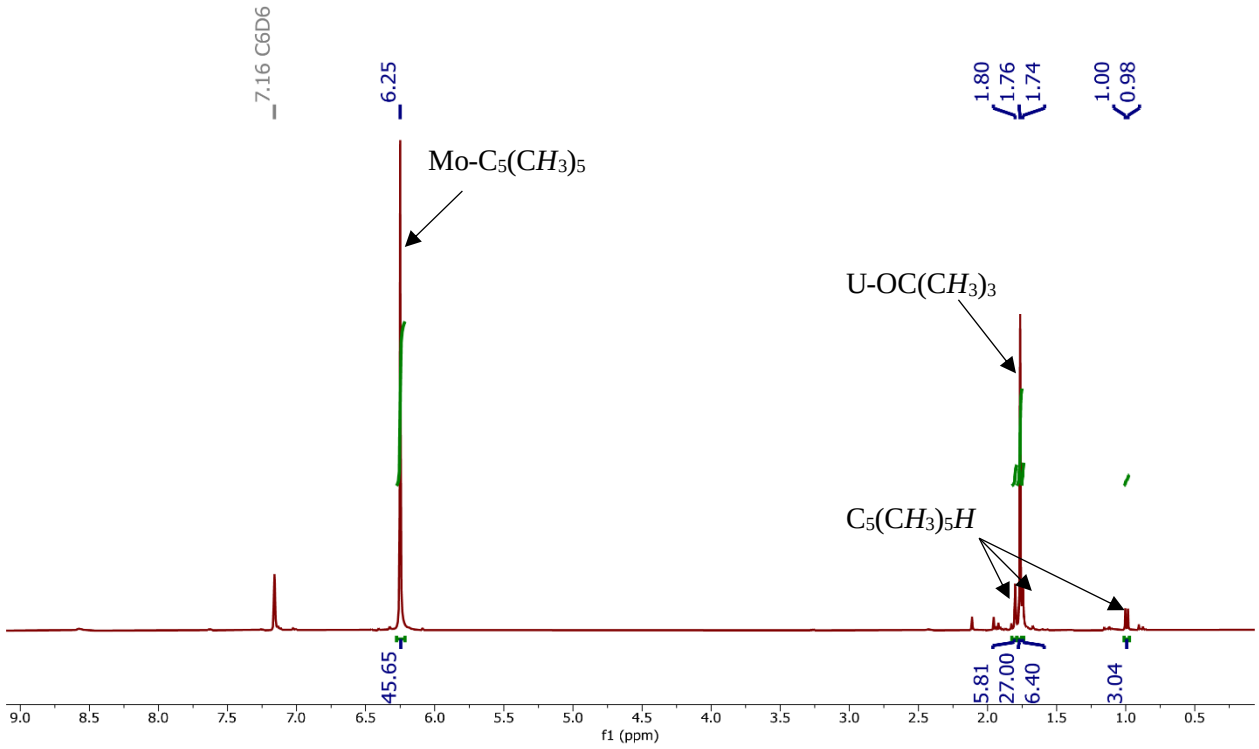

Figure S14. ^{1}H NMR spectrum (400 MHz) (with slow relaxation time) of the crude reaction mixture containing ($Cp^*_3Mo_3S_4$)UCp^* and 3 equivalent of *tert*-butanol in C_6D_6 [products: ($Cp^*_3Mo_3S_4$)U(O^tBu)$_3$ and Cp^*H].

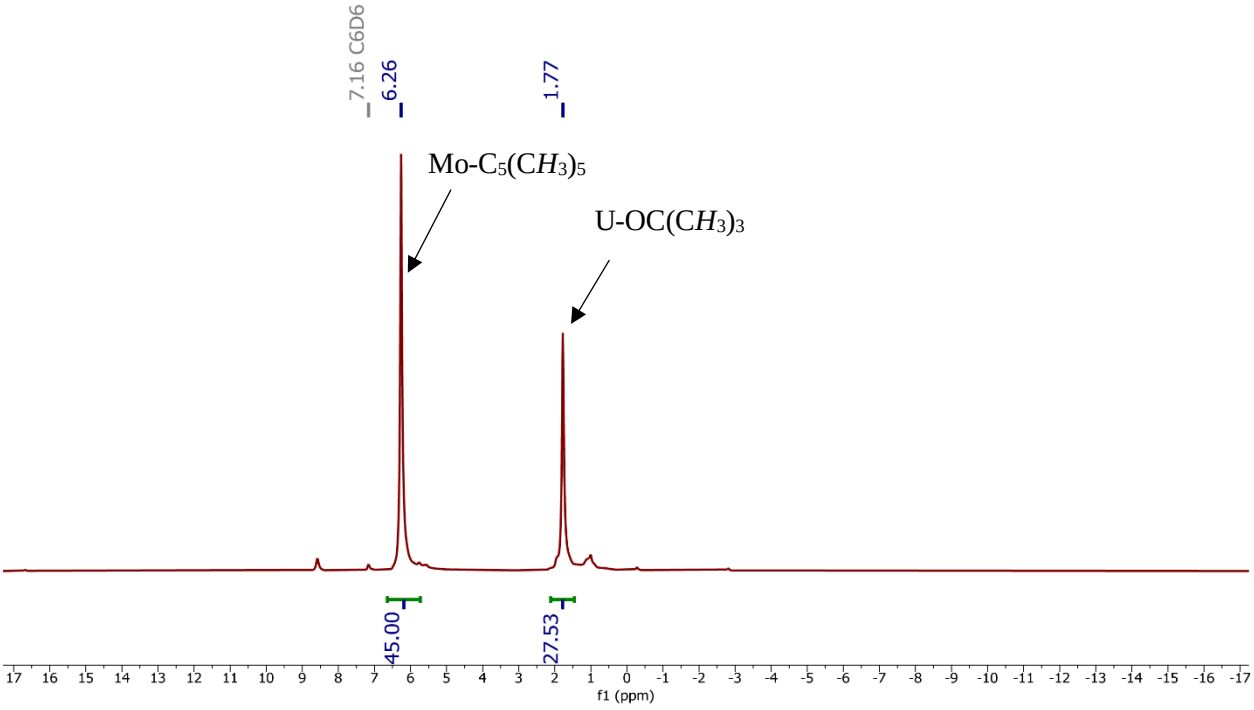

Figure S15. ^{1}H NMR spectrum (500 MHz) of the ($Cp^*_3Mo_3S_4$)U(O^tBu)$_3$ in C_6D_6.

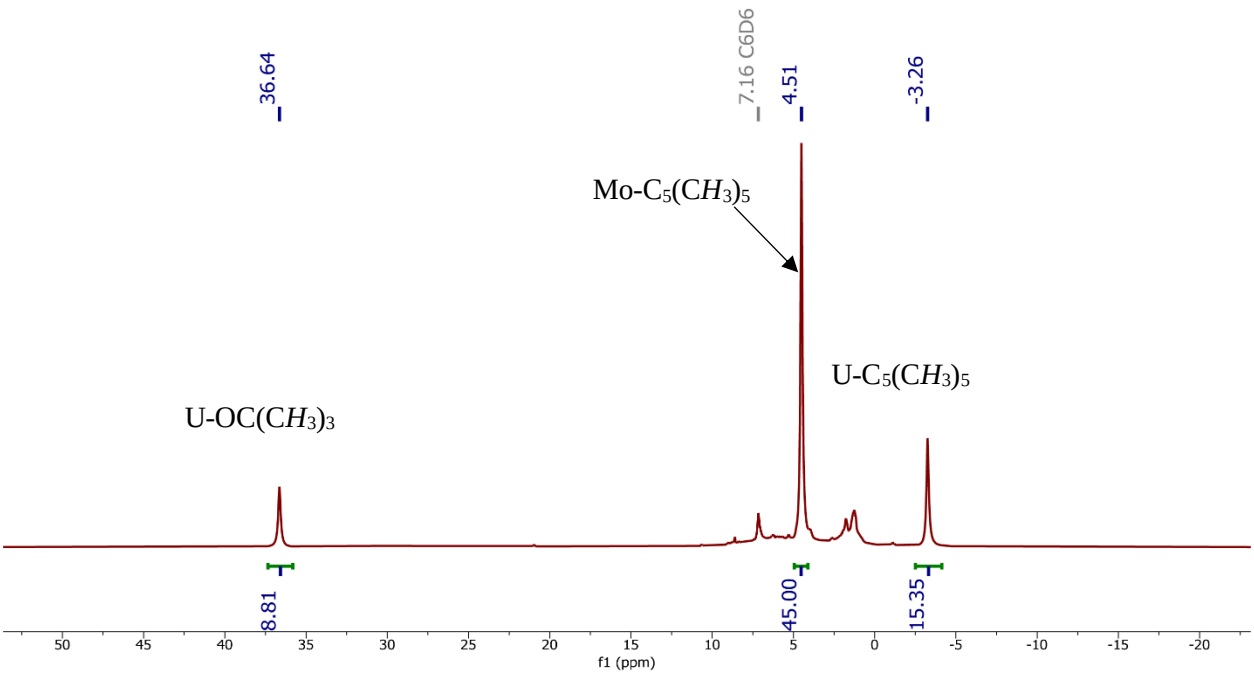

Figure S16. ^{1}H NMR spectrum (500 MHz) of (Cp*$_3$Mo$_3$S$_4$)Cp*U(O^{t}Bu) in C_6D_6.

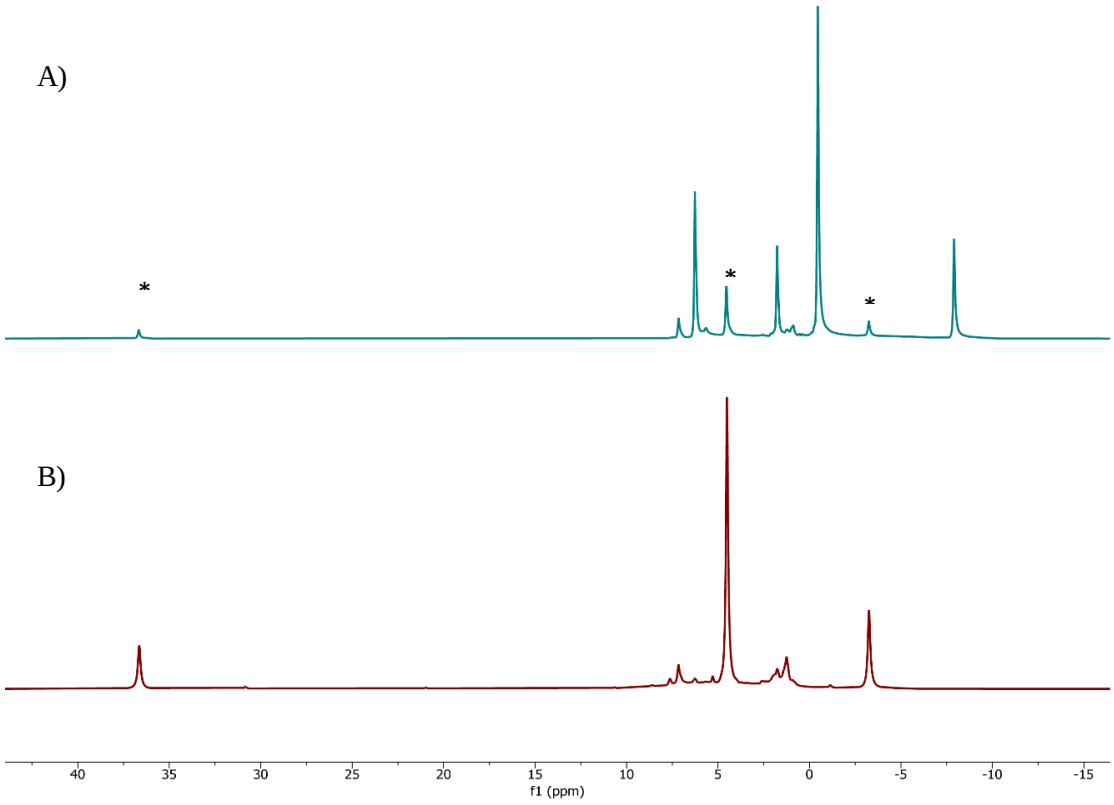

Figure S17. Stacked ^{1}H NMR spectra (500 MHz) of A) the reaction mixture containing (Cp*$_3$Mo$_3$S$_4$)UCp* and 1 equivalent of *tert*-butanol and B) (Cp*$_3$Mo$_3$S$_4$)Cp*U(O^{t}Bu) in C_6D_6 [* signals represent the minor component (Cp*$_3$Mo$_3$S$_4$)Cp*U(O^{t}Bu) in the reaction mixture (A)].

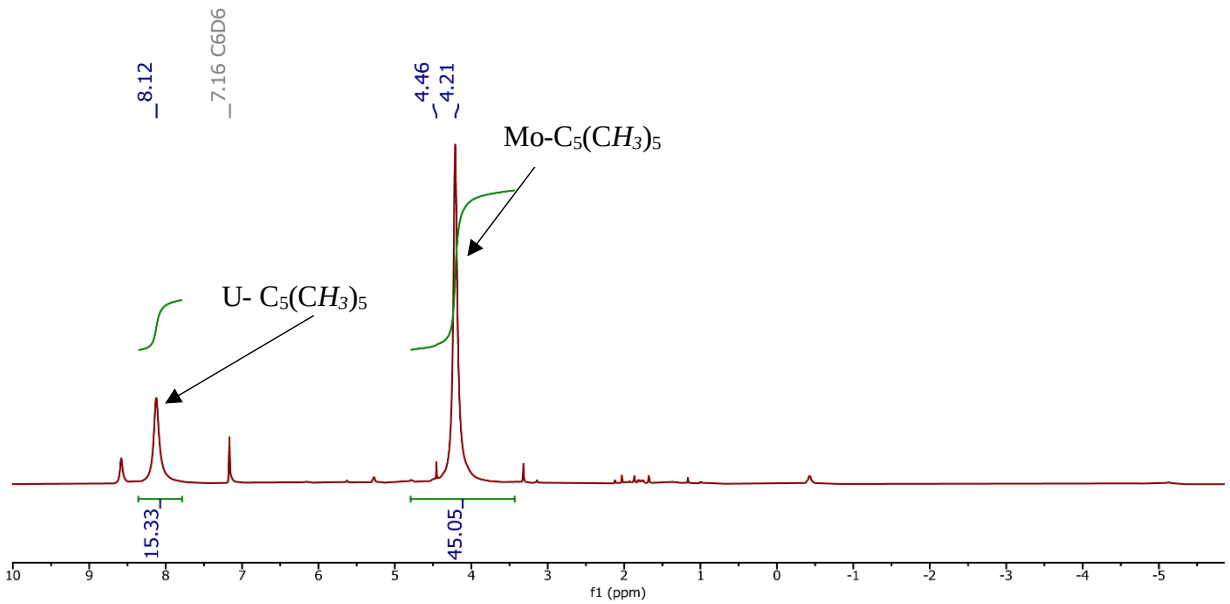

Figure S18. ^{1}H NMR spectrum (400 MHz) of $(Cp^*_3Mo_3S_4)Cp^*U(OC(CF_3)_3)$ in C_6D_6 (The signal at 4.46 ppm is assigned to H_2).

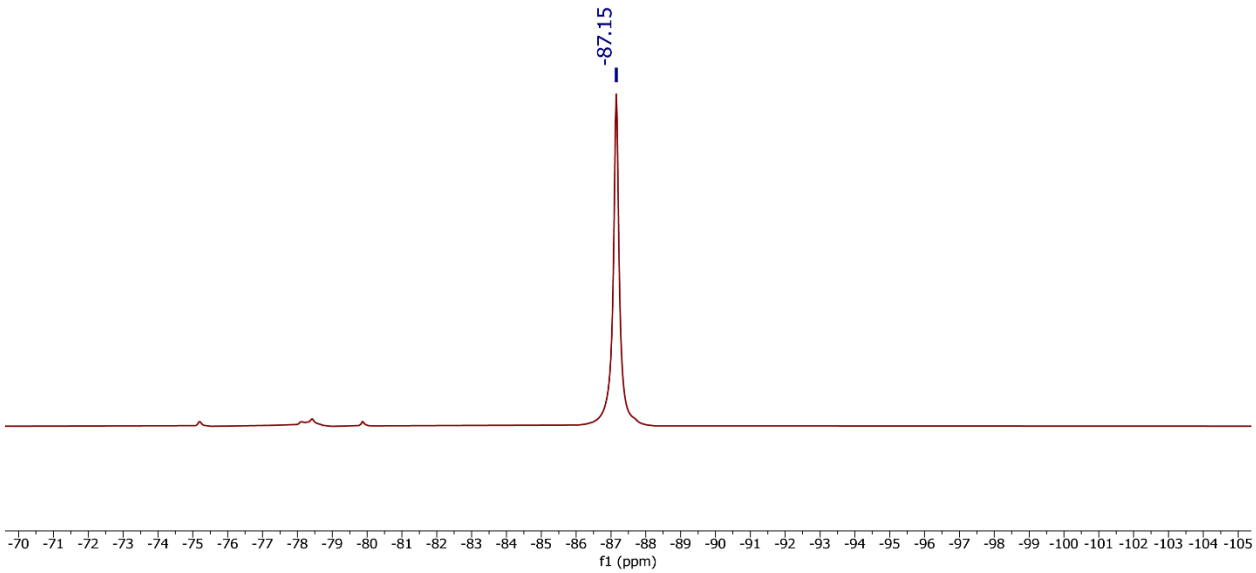

Figure S19. $^{19}F\{^{1}H\}$ NMR spectrum of the $(Cp^*_3Mo_3S_4)Cp^*U(OC(CF_3)_3)$ in C_6D_6.