

Supporting Information to Accompany:

Ruthenium–Thymine Acetate binding modes: Experimental and Theoretical Studies

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Table S1. Crystal data and structure refinement for compound *cis-2*

Compound	<i>cis-2</i>
Formula	C ₅₁ H ₄₄ N ₄ O ₉ P ₂ Ru
Fw	1019.91
T, K	296
λ , Å	0.71073
Crystal symmetry	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	14.895(3)
<i>b</i> , Å	13.501(3)
<i>c</i> , Å	25.513(5)
α	90
β	100.836(2)
γ	90
Cell volume, Å ³	5039.4(18)
<i>Z</i>	4
<i>D_c</i> , Mg m ⁻³	1.344
μ (Mo-K α), mm ⁻¹	0.432
F(000)	2096
Crystal size/ mm	0.25 x 0.20 x 0.15
θ limits, °	1.474 - 25.013
Reflections collected	44083
Unique obs. Reflections [<i>F_o</i> > 4 σ (<i>F_o</i>)]	8809 [R(int) = 0.1153]
Goodness-of-fit-on <i>F</i> ²	0.939
<i>R</i> ₁ (<i>F</i>) ^a , <i>wR</i> ₂ (<i>F</i> ²) [<i>I</i> > 2 σ (<i>I</i>)]	0.0706, 0.1068
Largest diff. peak and hole, e. Å ⁻³	0.455 and -0.378

^a) $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. ^b) $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + F_c^2)/3$.

Table S2. Most relevant hydrogen bonds for *cis-2* [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)···O(7)#1	0.86	2.12	2.798(9)	134.8
N(4)-H(4N)···O(4)#1	0.86	2.05	2.893(10)	164.8

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2, y-1/2, -z+1/2 #2 -x+1, -y+1, -z

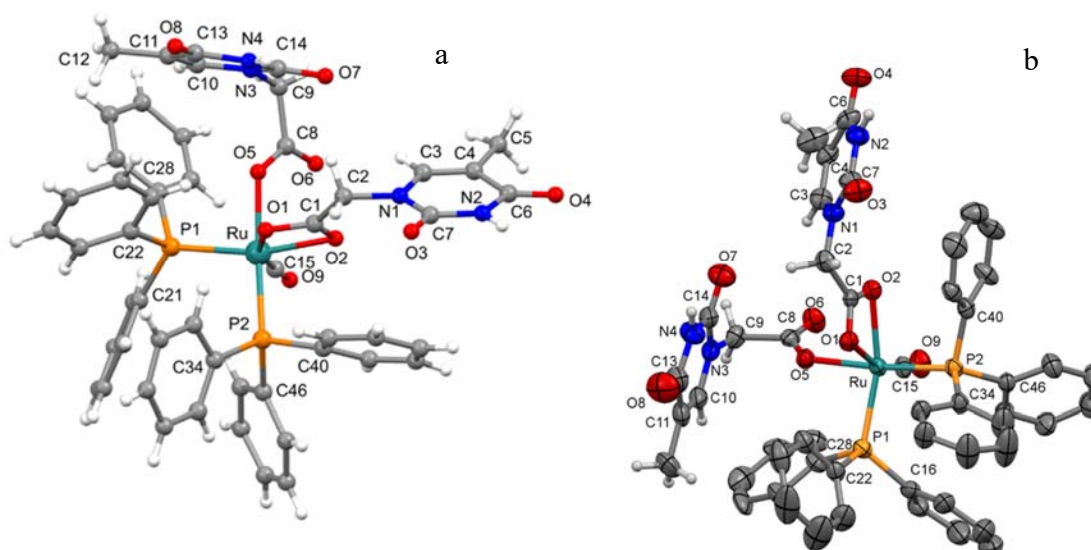


Figure S1. a) Molecular structure of *cis-2* with the atom labelling, b) ORTEP drawing of *cis-2* (thermal ellipsoids are drawn at the 30% of the probability level) with the atom labelling scheme. The phenyl H atoms have been omitted for the sake of clarity.

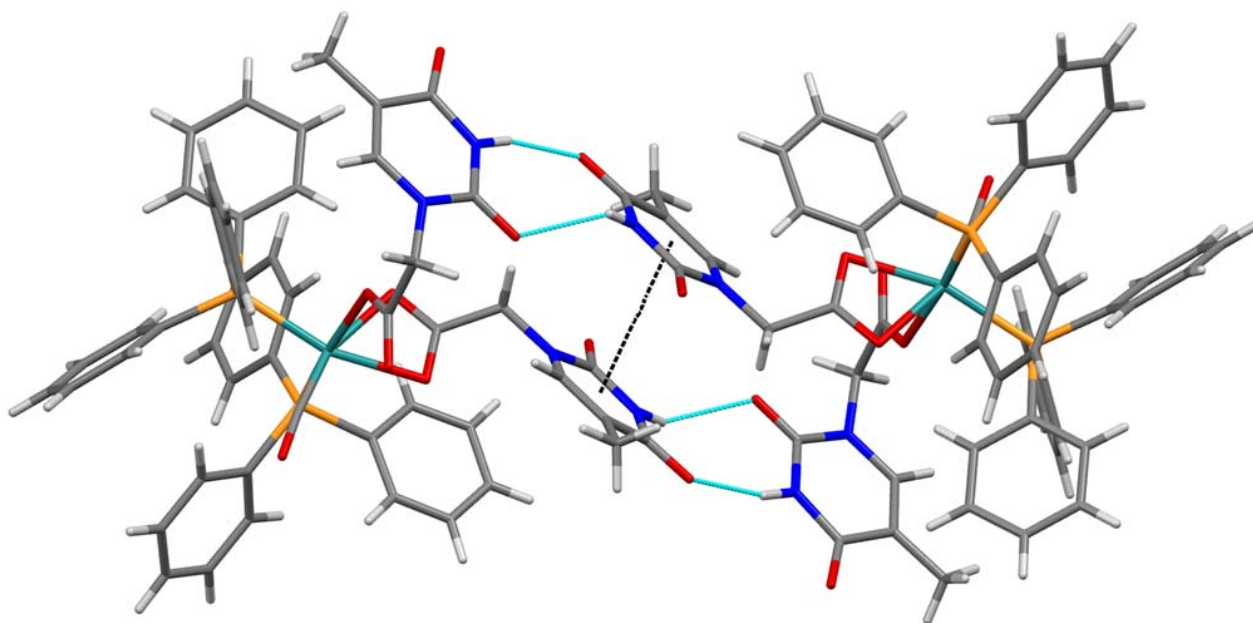


Figure S2. Molecular structure of *cis-2* with π - π stacking and Watson-Crick intermolecular interaction

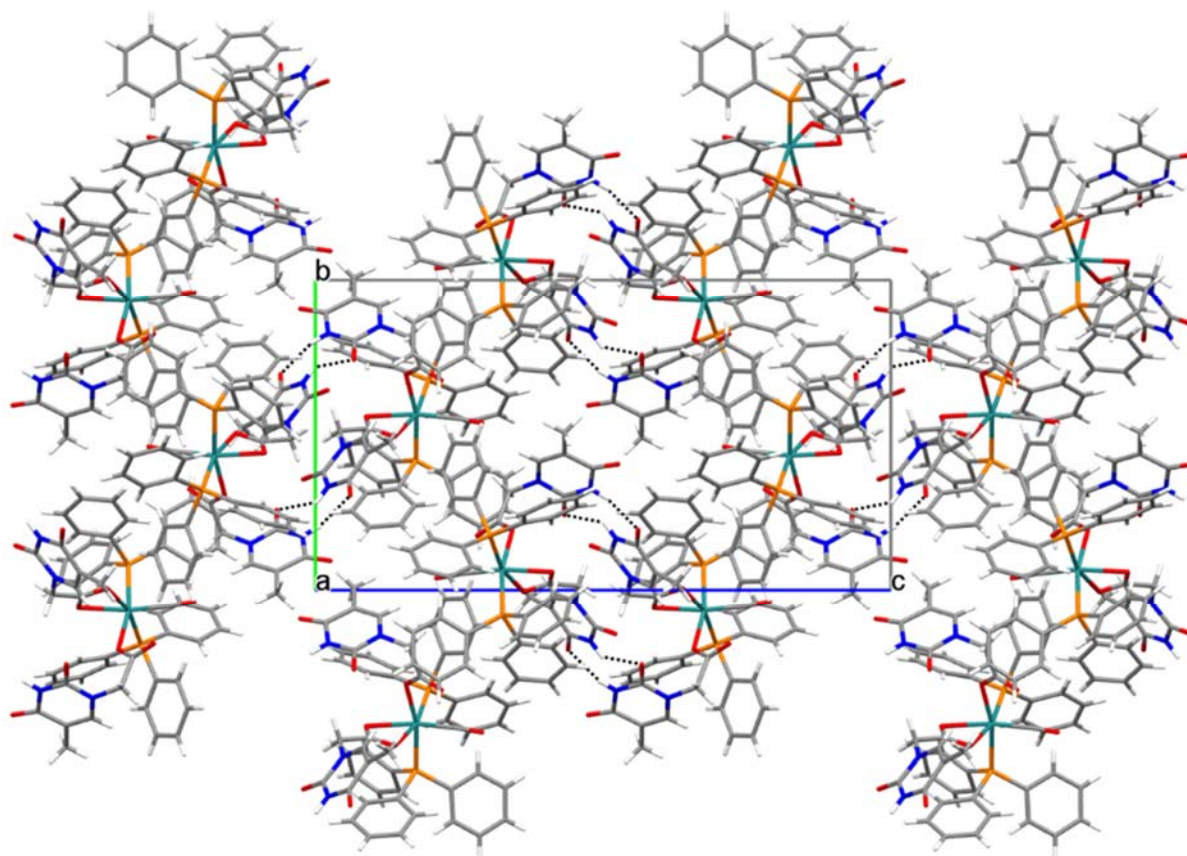


Figure S3. View down. Fragment of the crystal packing of complex **2** illustrating the intermolecular H bonding pattern. For the sake of clarity only the H atoms engaged in H bonds are shown. Ball and stick representation is used for the dimer arising by the strong N-H $\cdots$ O hydrogen bonding and for the atoms connected to it. H bonds are shown with blue dashed lines. The *a* axis of the crystal packing of *cis*-**2**. Black dotted lines indicate the intermolecular N-H $\cdots$ O hydrogen bonds.

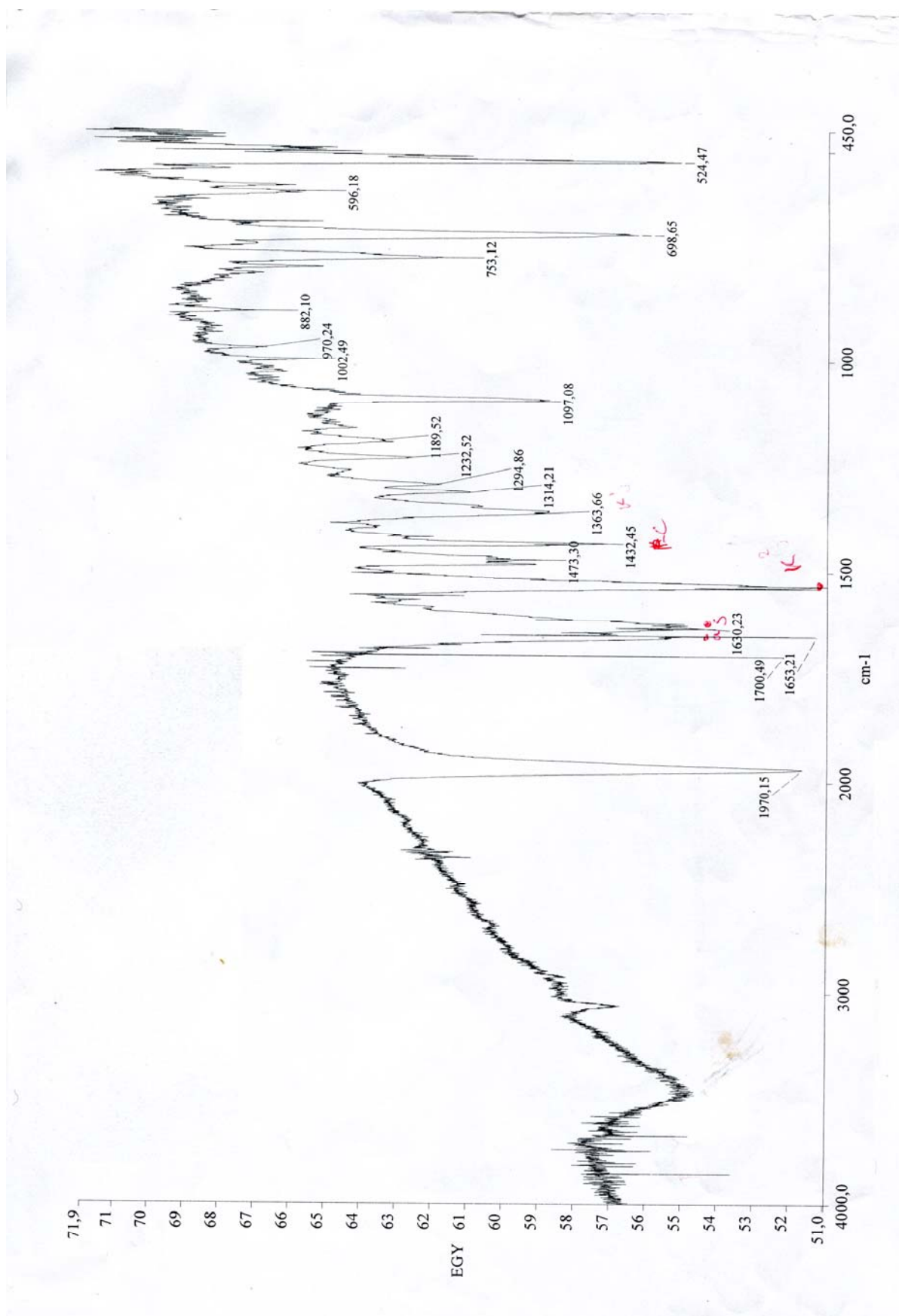


Figure S4. FTIR of of *trans*-{Ru(CO)(PPh₃)₂[κ¹(O)THAc][κ²(O,O)THAc]} **2**

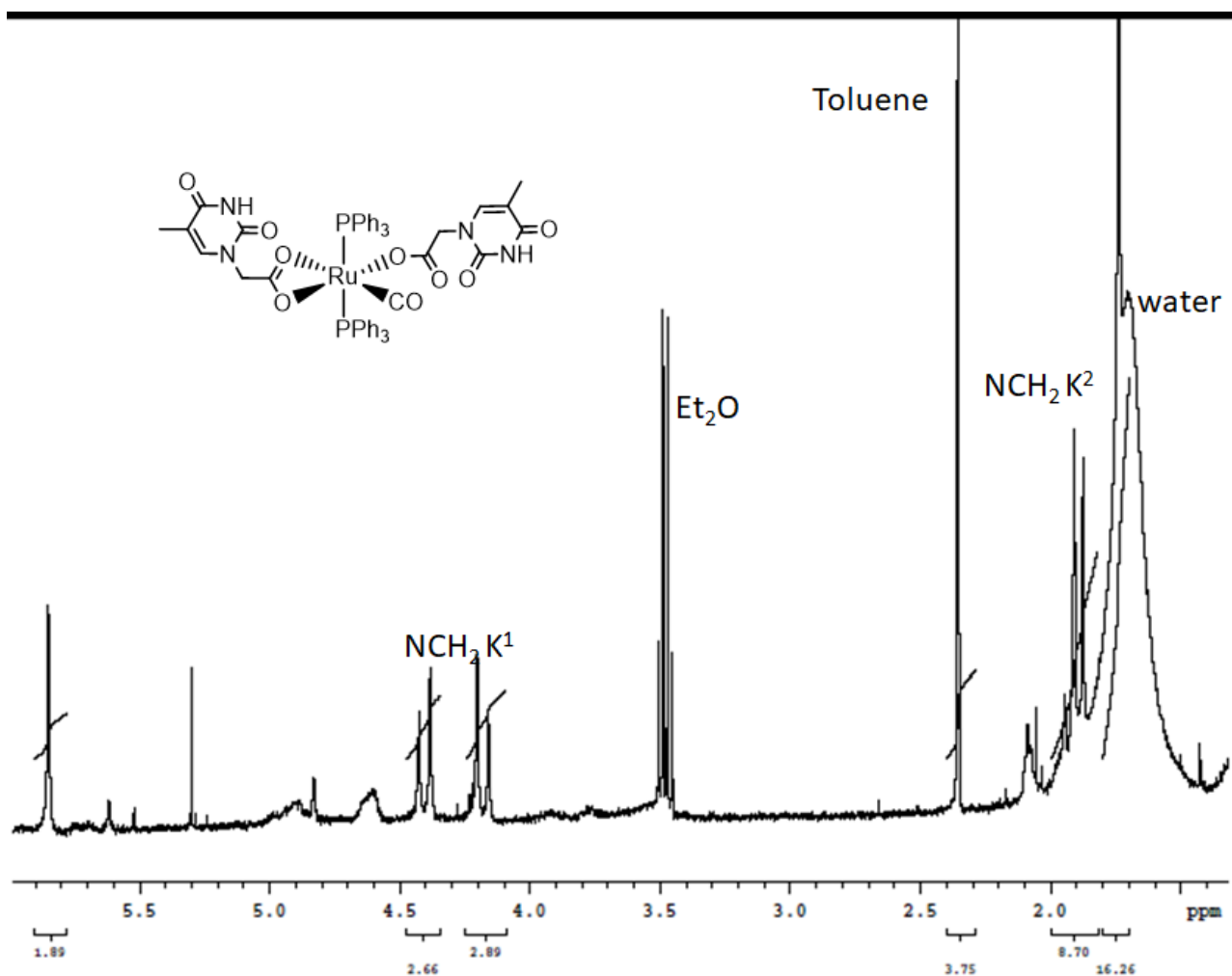


Figure S5a. ^1H -NMR (400 MHz) of *trans*- $\{\text{Ru}(\text{CO})(\text{PPh}_3)_2[\kappa^1(\text{O})\text{THAc}][\kappa^2(\text{O},\text{O})\text{THAc}]\}$ **2** in CDCl_3

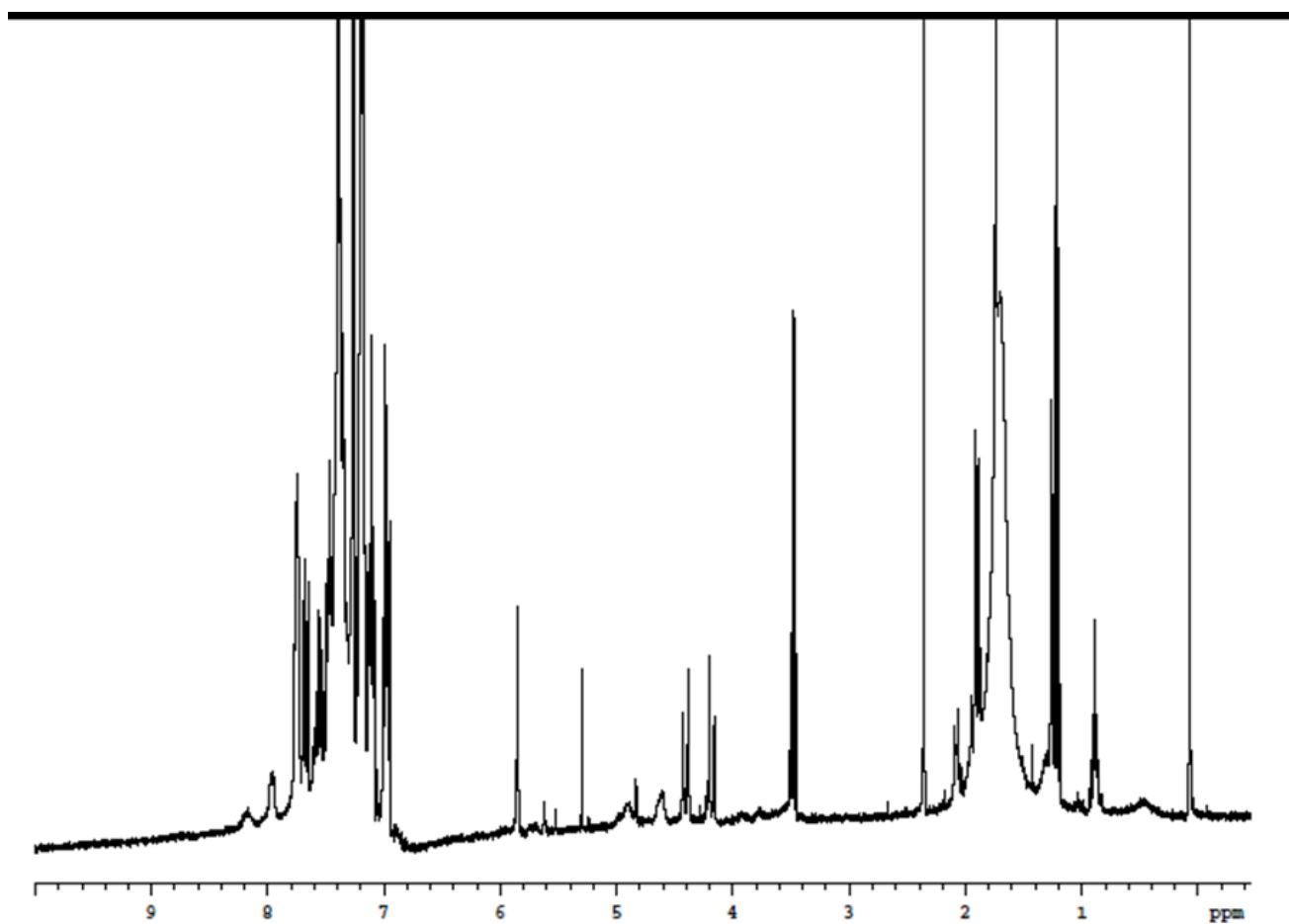


Figure S5b. ¹H-NMR (400 MHz) of *trans*-{Ru(CO)(PPh₃)₂[κ¹(O)THAc][κ²(O,O)THAc]} **2** in CDCl₃

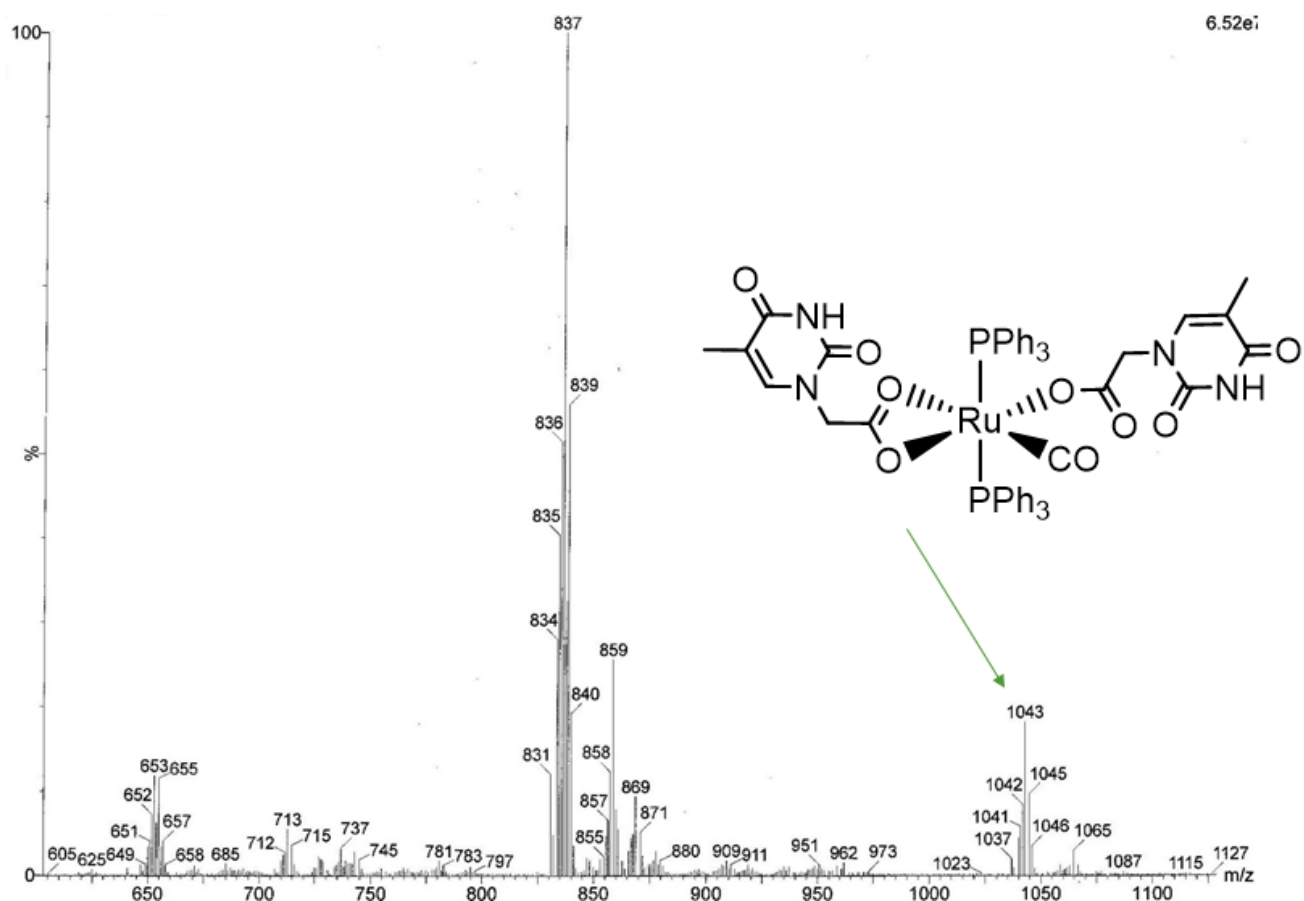


Figure S6. ESI-MS of of $\text{cis-}\{\text{Ru}(\text{CO})(\text{PPh}_3)_2[\kappa^1(\text{O})\text{THAc}][\kappa^2(\text{O},\text{O})\text{THAc}]\}$ 2

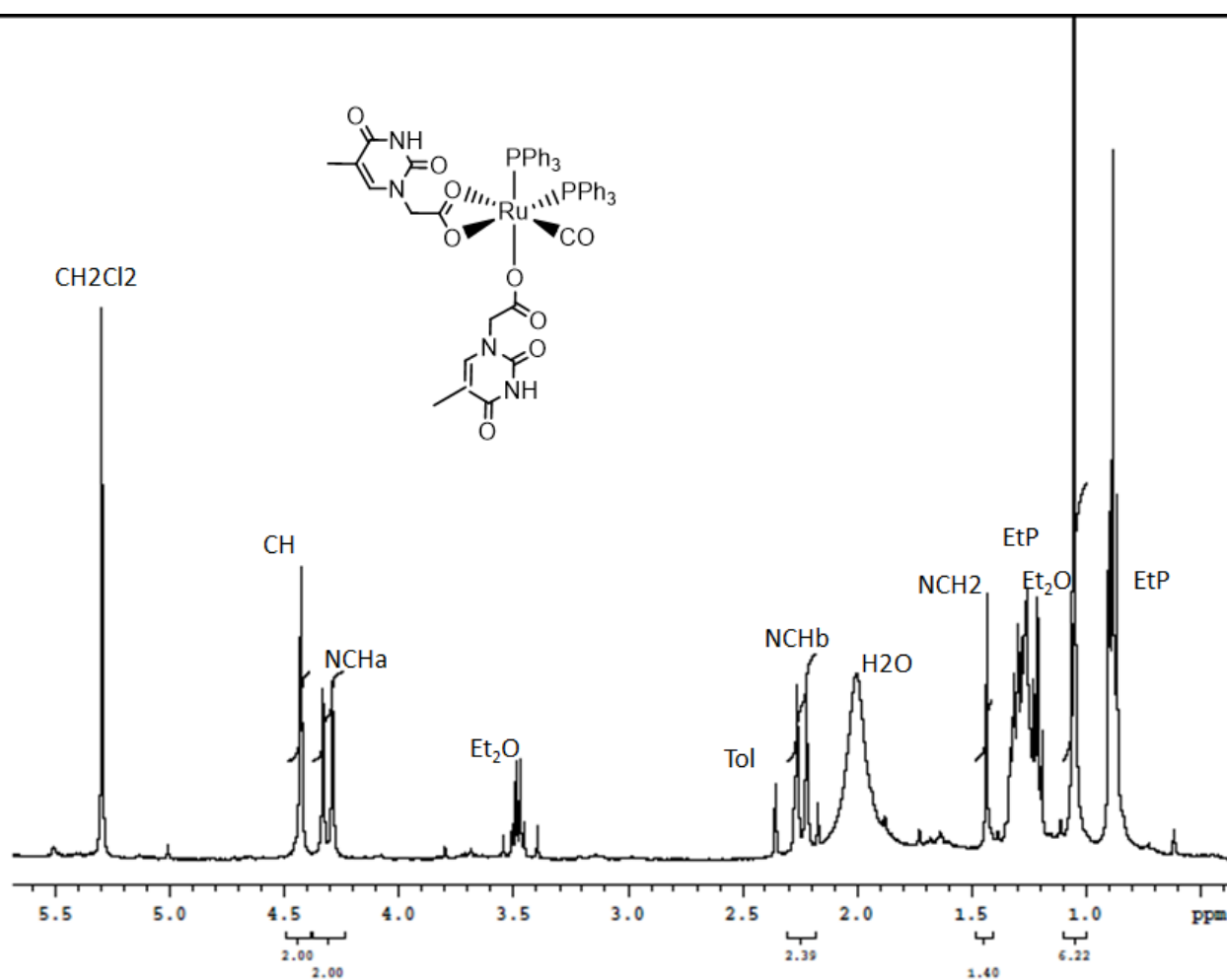
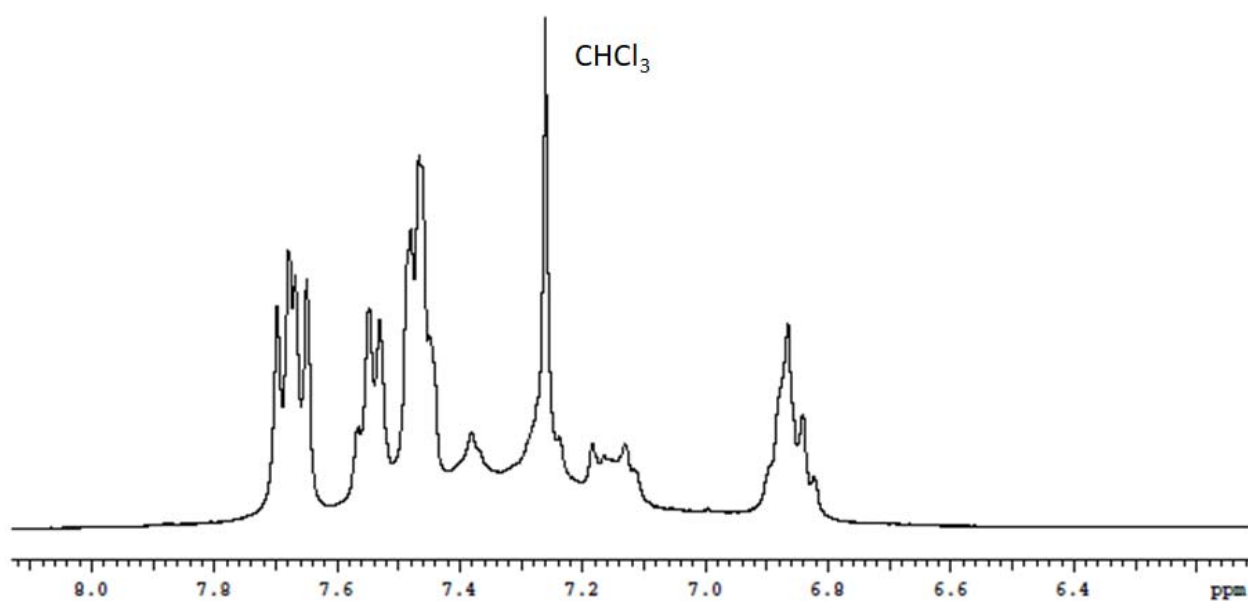


Figure S7a. ¹H-NMR (400 MHz) of *cis*-{Ru(CO)(PPh₃)₂[κ¹(O)THAc][κ²(O,O)THAc]} **2** in CDCl₃



The water present in the spectrum is proportional to the 30% of CDCl₃

Figure S7b. ^1H -NMR (400 MHz) of *cis*-{Ru(CO)(PPh₃)₂[κ^1 (O)THAc][κ^2 (O,O)THAc]} **2** aromatic region in CDCl₃

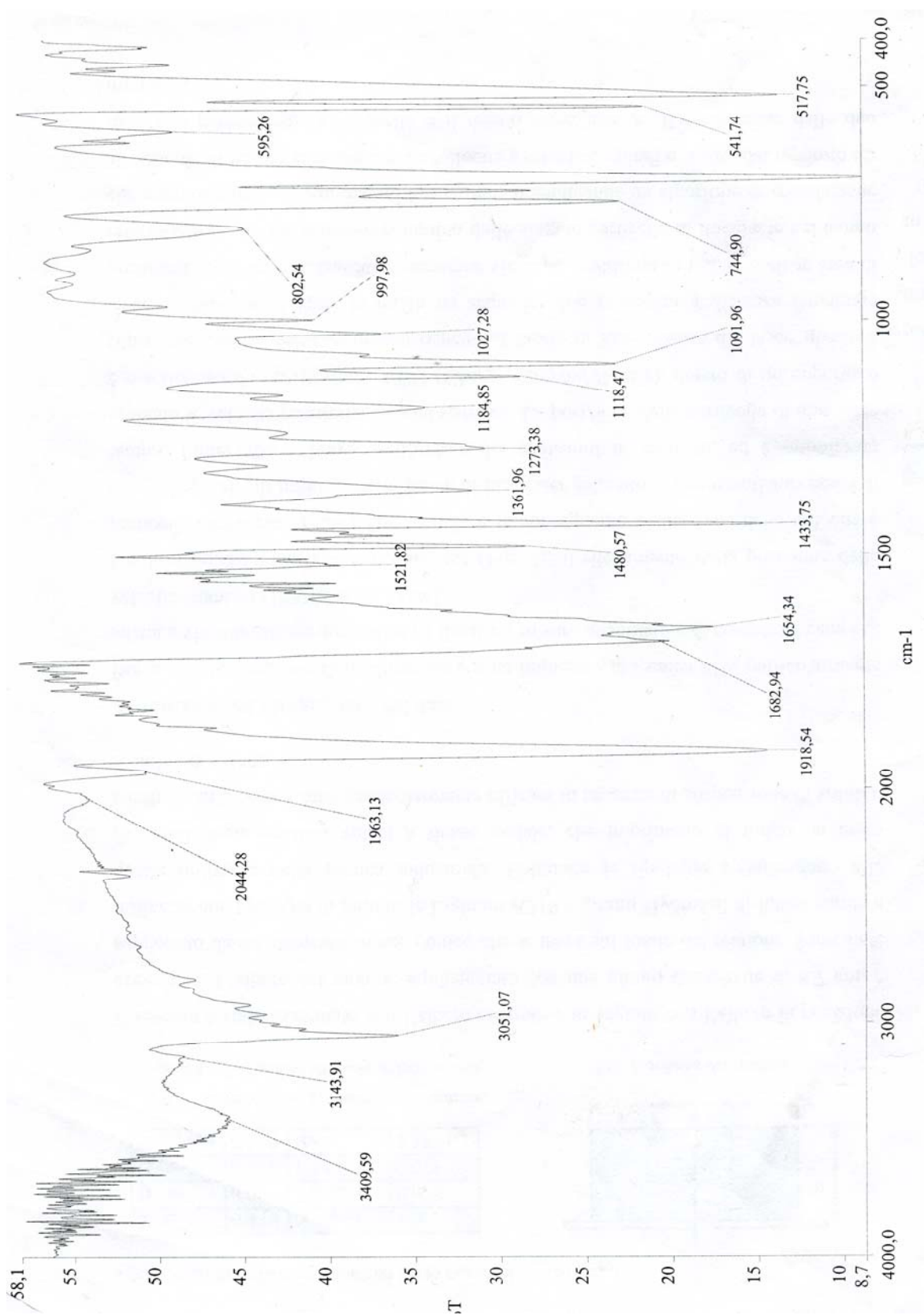


Figure S8. FTIR spectrum of **3 a,b**

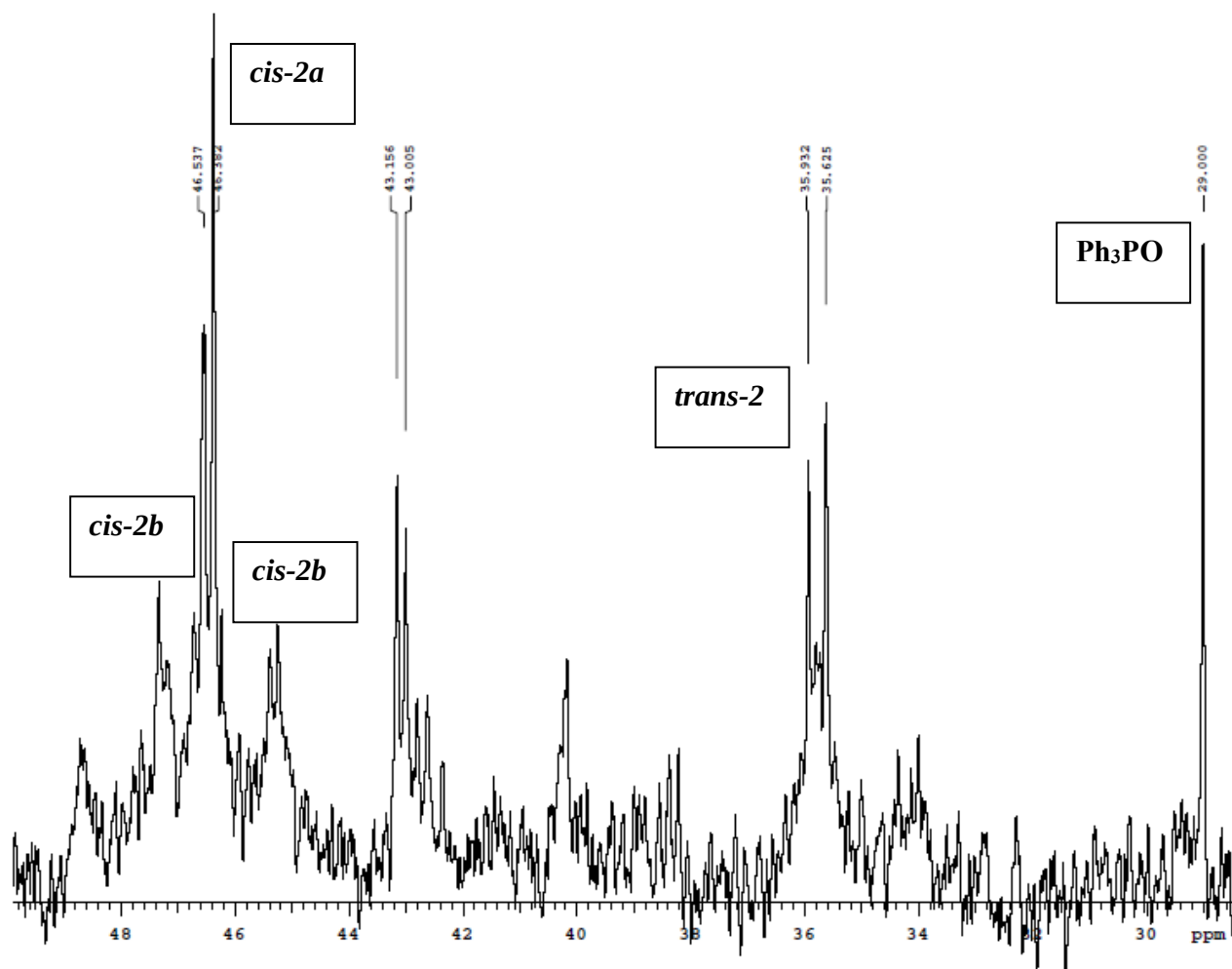


Figure S9. ^{31}P -NMR (161 MHz) of **2** in CDCl_3

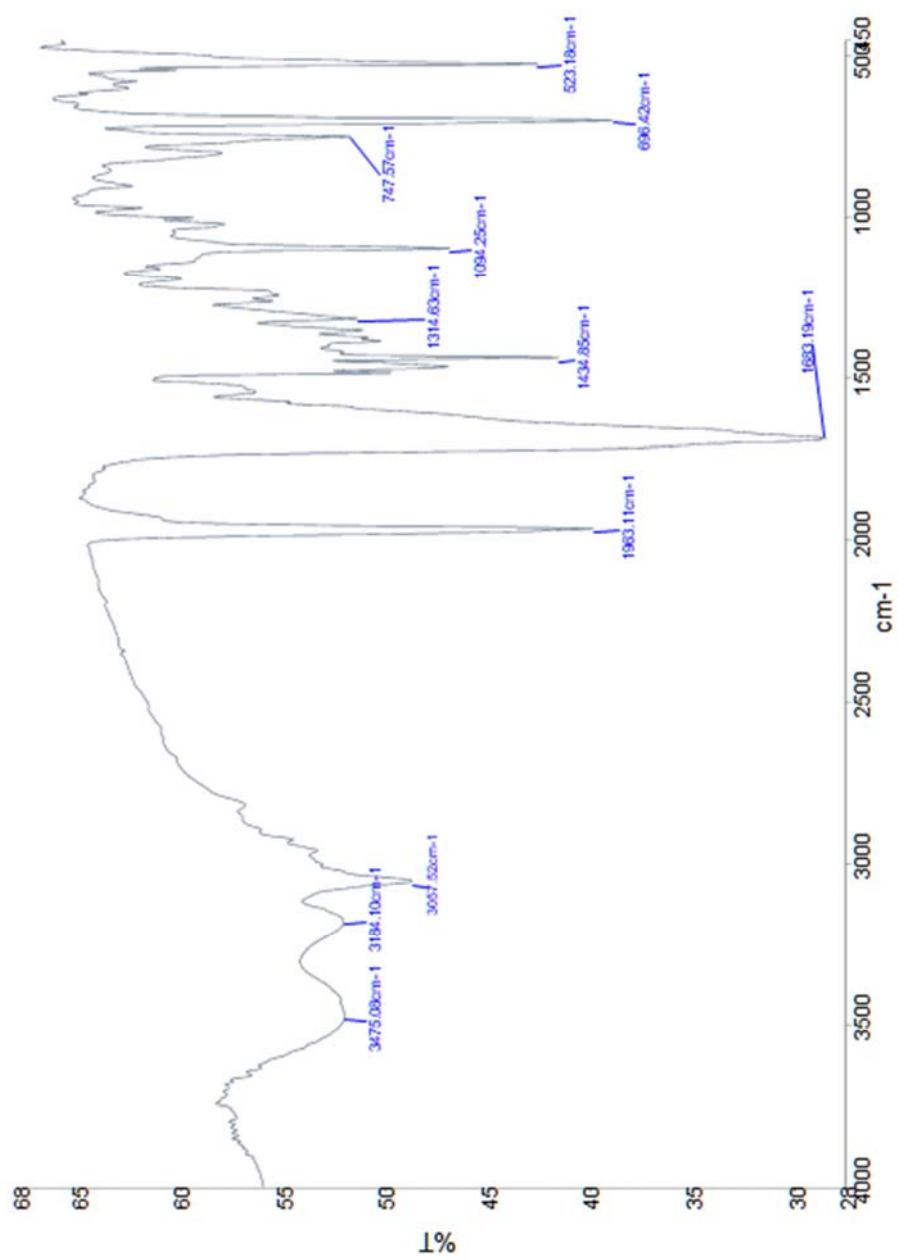


Figure S10. FT-IR (KBr) $k^2(O,O)\text{-RuH(CO)(THAc)(PPh}_3)_2$ 4

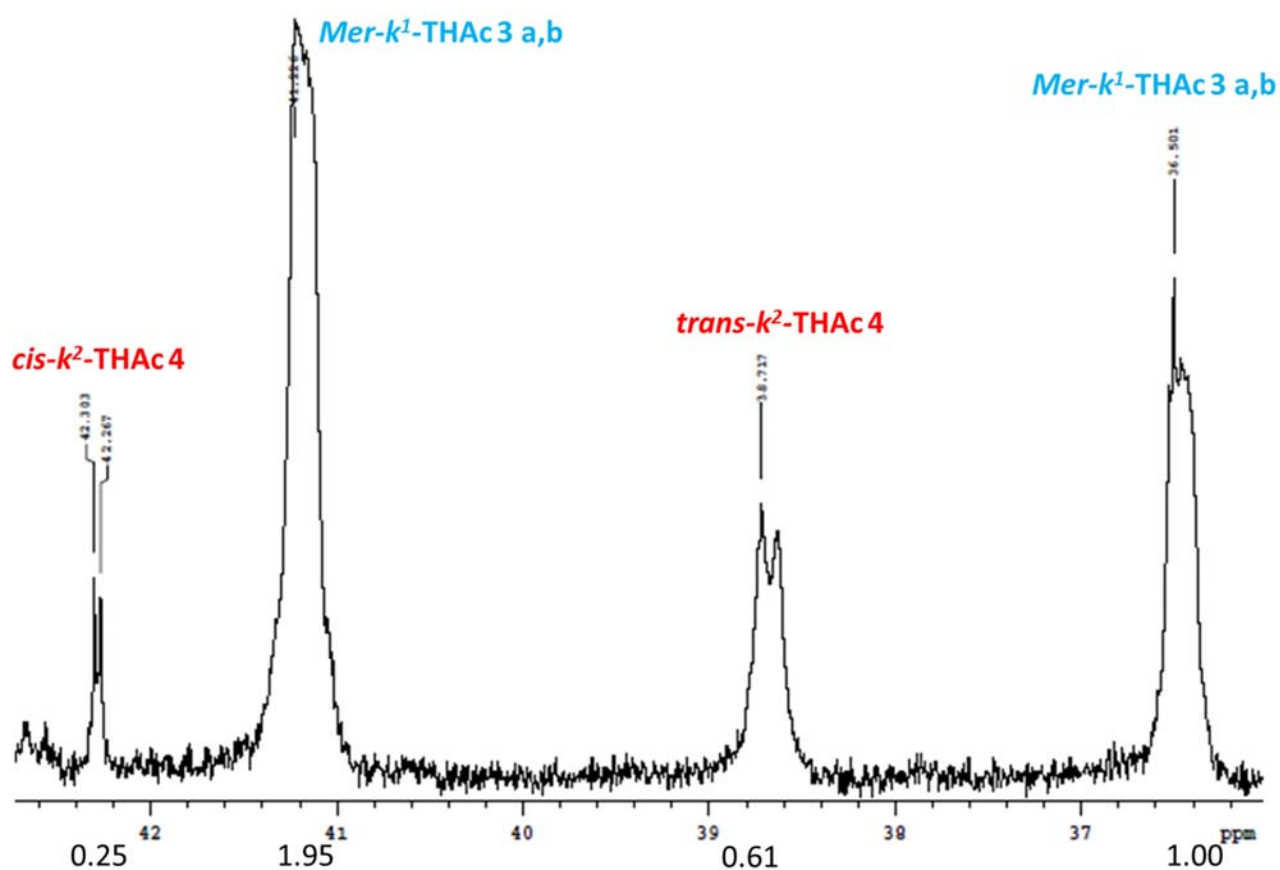


Figure S11a. $^{31}\text{P}\{^1\text{H}\}$ -NMR (161,9 MHz) $k^1(\text{O})\text{-}[\text{RuH}(\text{CO})(\text{THAc})(\text{PPh}_3)_3]$ **3** + $k^2(\text{O},\text{O})\text{-RuH}(\text{CO})(\text{THAc})(\text{PPh}_3)_2$ **4** in (3:4=3:0,8) CDCl_3

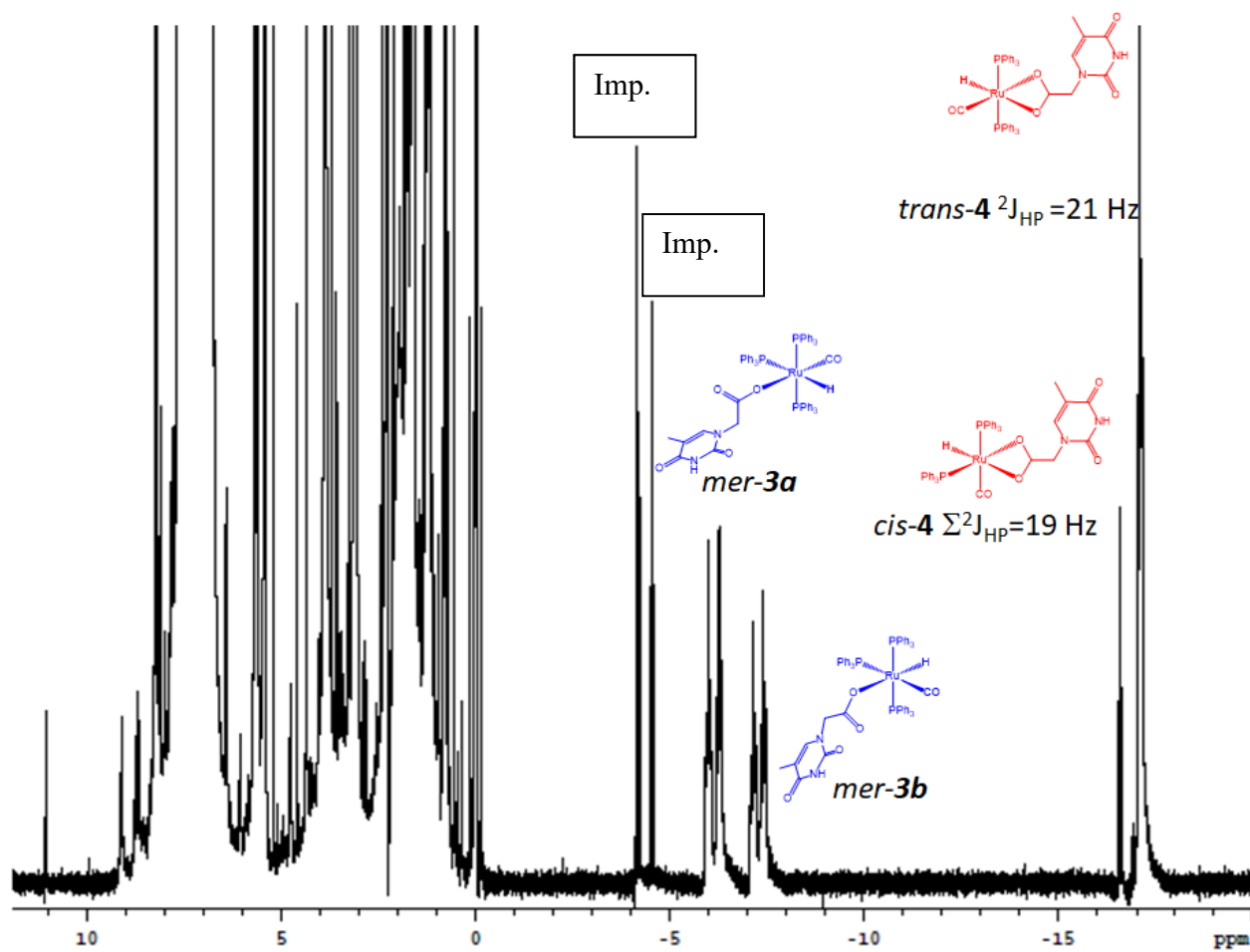


Figure S11b. ^1H -NMR spectrum of **3** + **4** (ratio 3:2) in CDCl_3

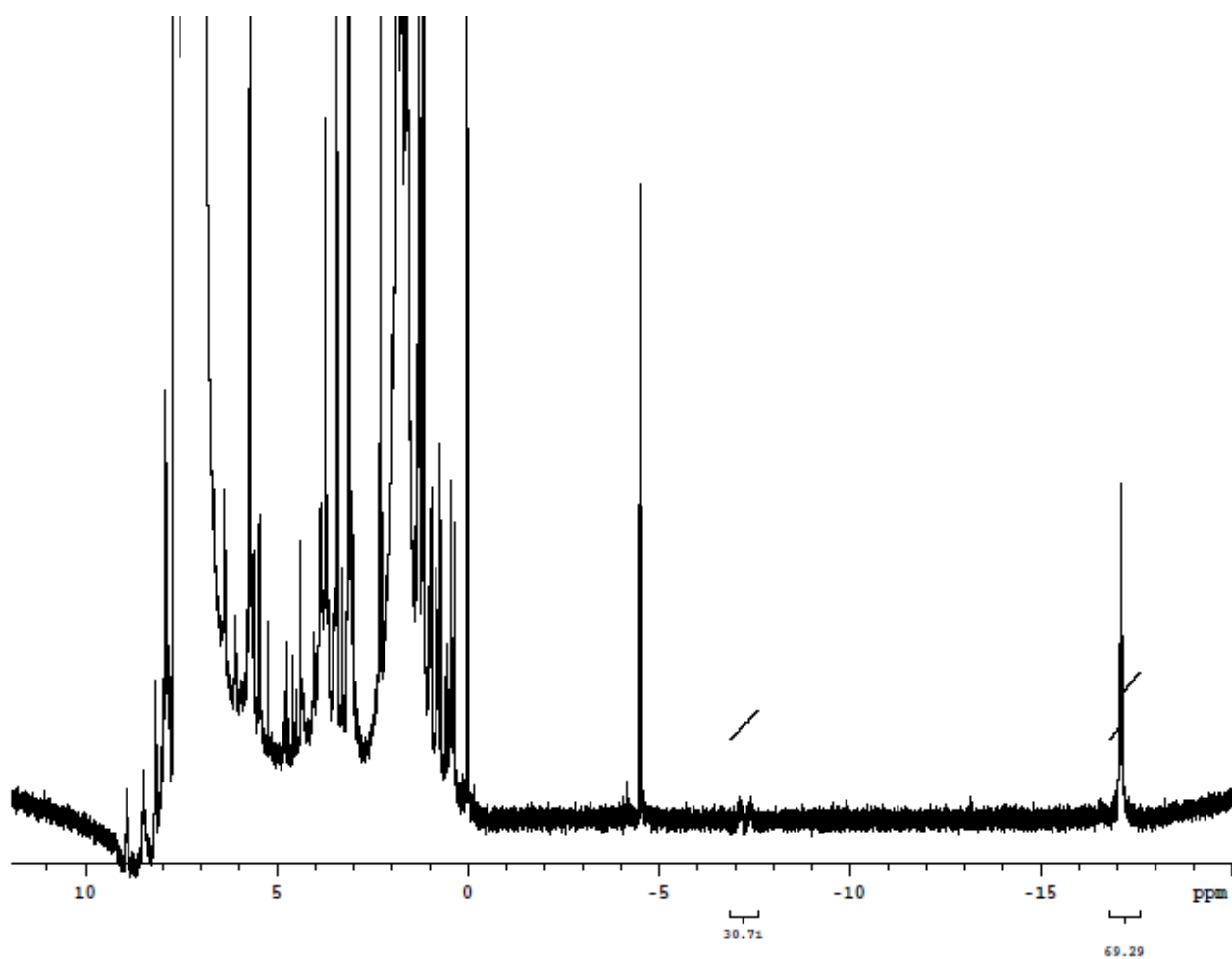


Figure S11c. ^1H -NMR spectrum of **3** + **4** (ratio 3:7) in CDCl_3

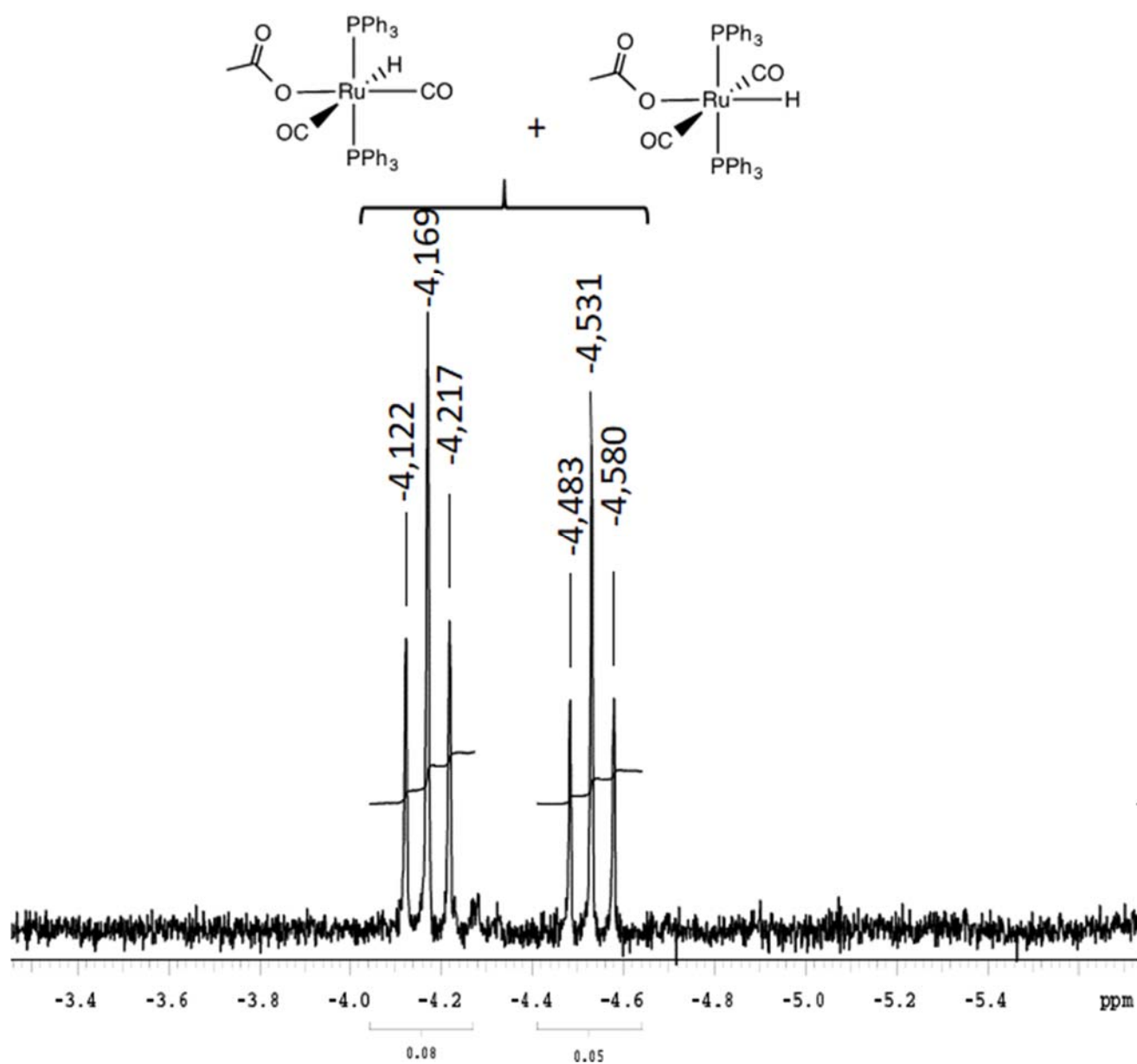


Figure 11d. Complexes formed as impurities during the preparative reduction of starting material **1**

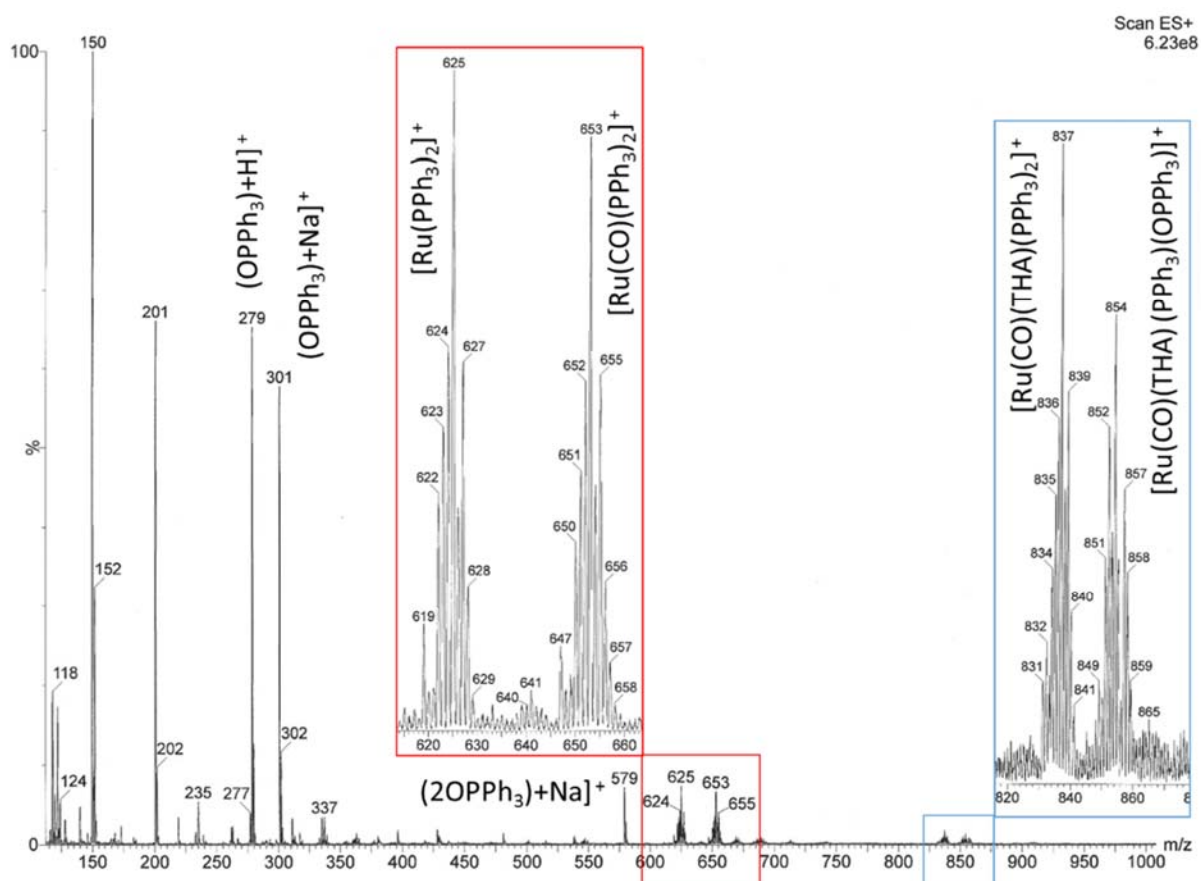


Figure S12. ESI-MS (MeOH) of $\kappa^2(\text{O},\text{O})\{\text{HRu}(\text{CO})(\text{PPh}_3)_2[\kappa^2(\text{O},\text{O})\text{THAc}]\}$ **4**

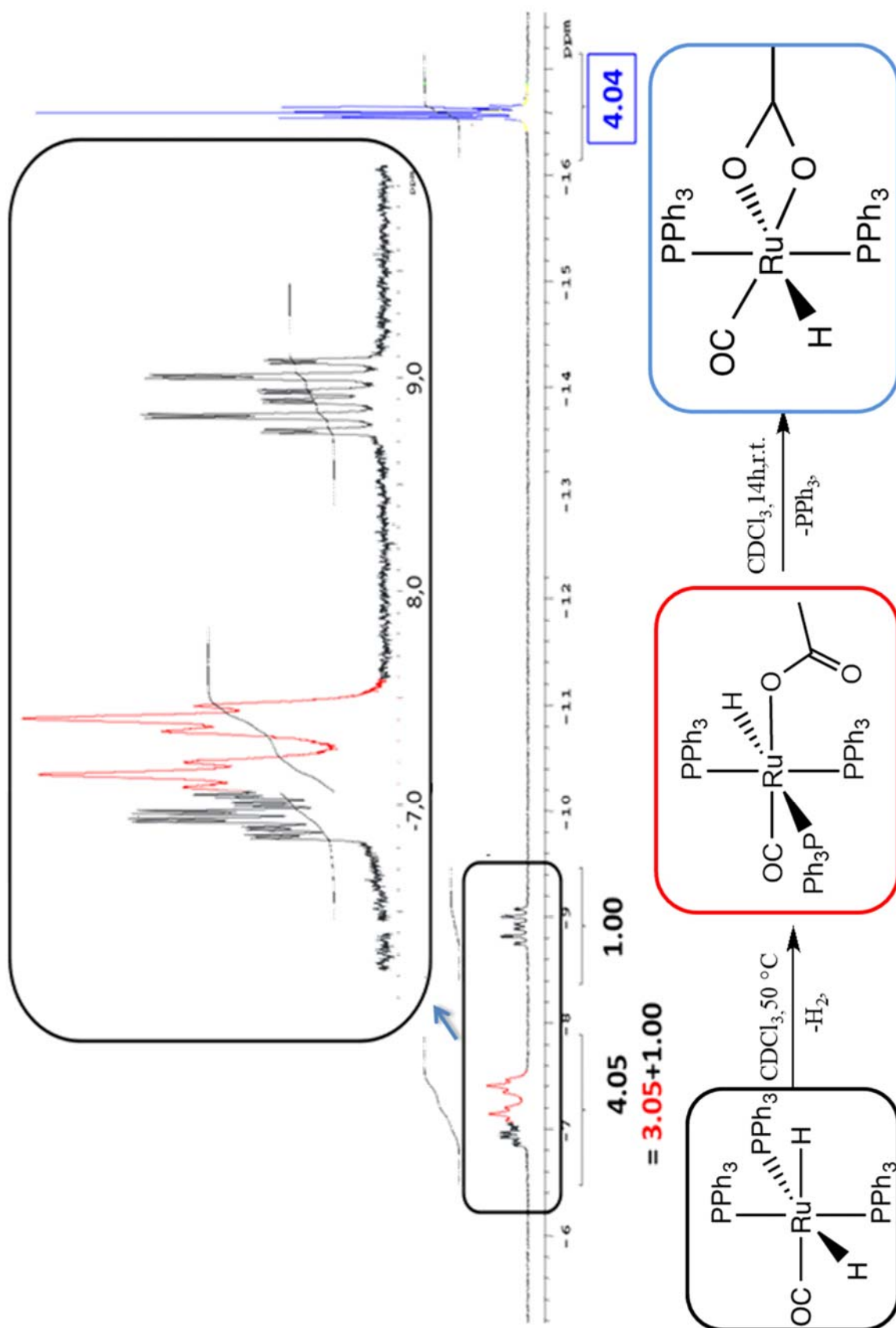


Figure S13. ^1H -NMR hydride region spectrum of **1+5+6** in CDCl_3

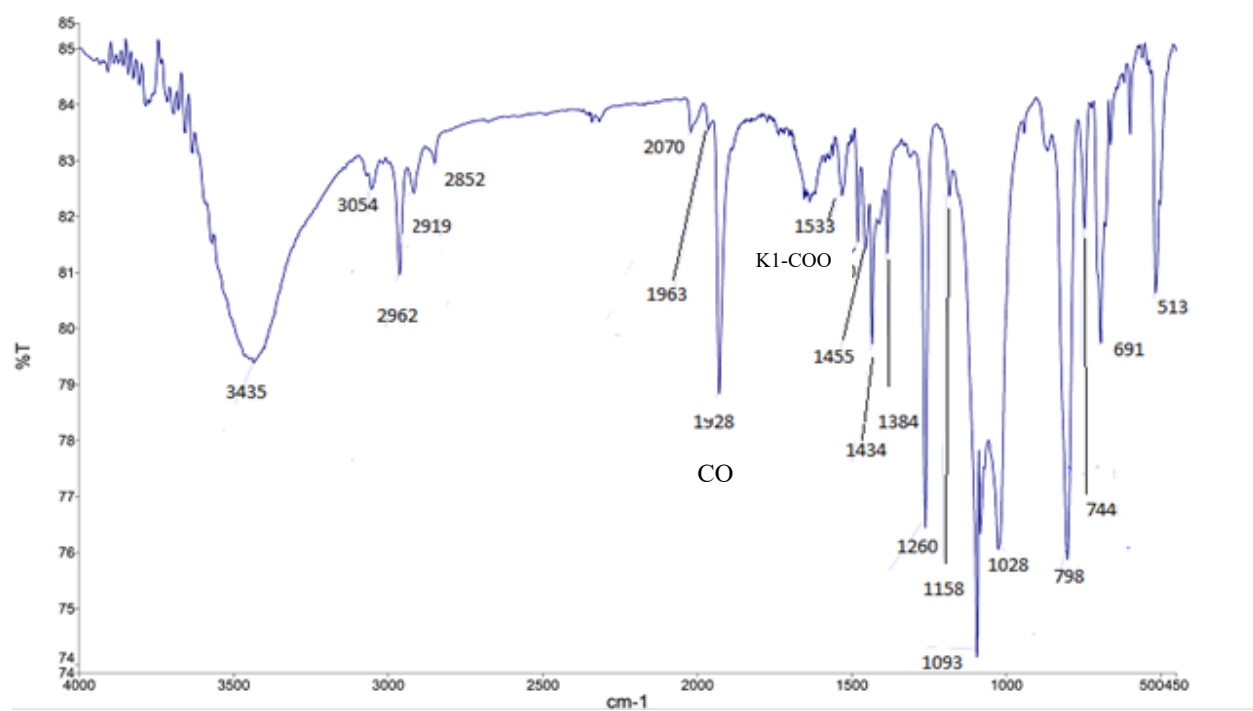


Figure S14. FTIR of compound $\kappa^1(\text{O})\text{Ac}[\text{RuH}(\text{CO})(\text{PPh}_3)_3]$ 5

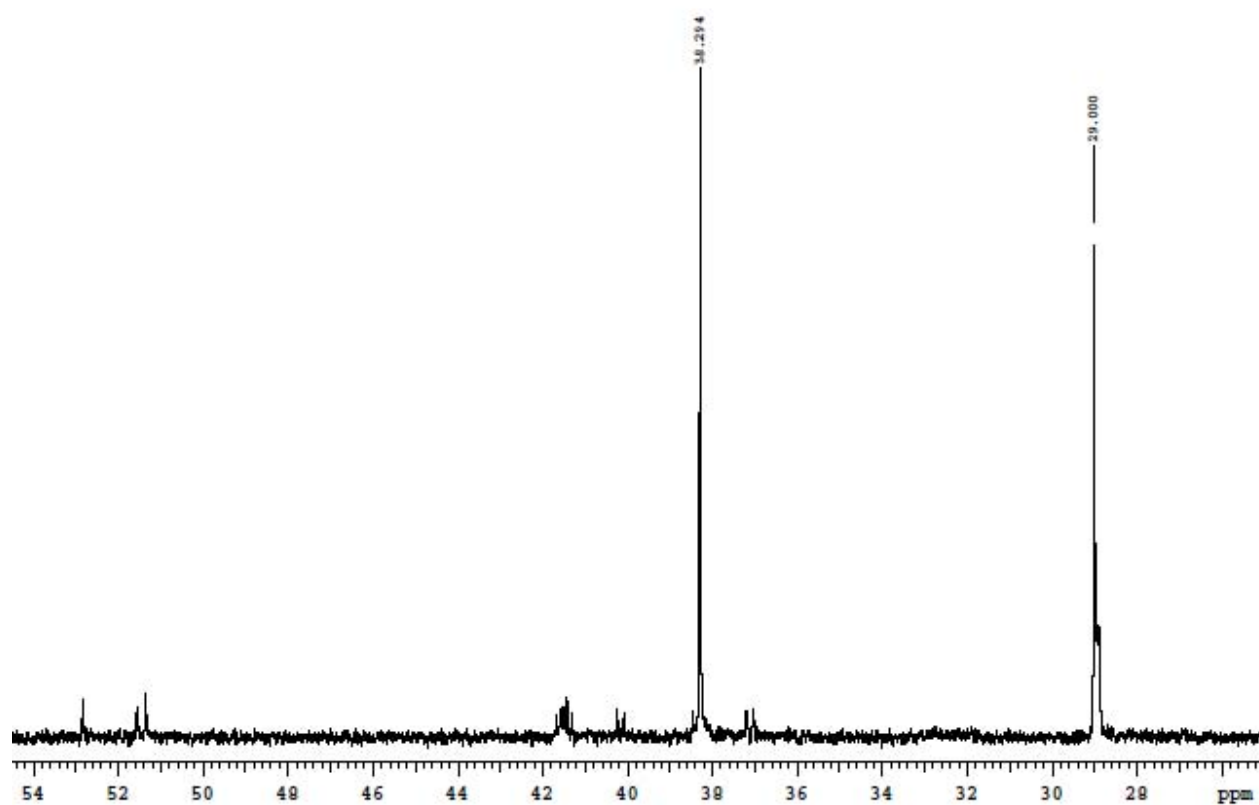


Figure S15a. $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **6** species.

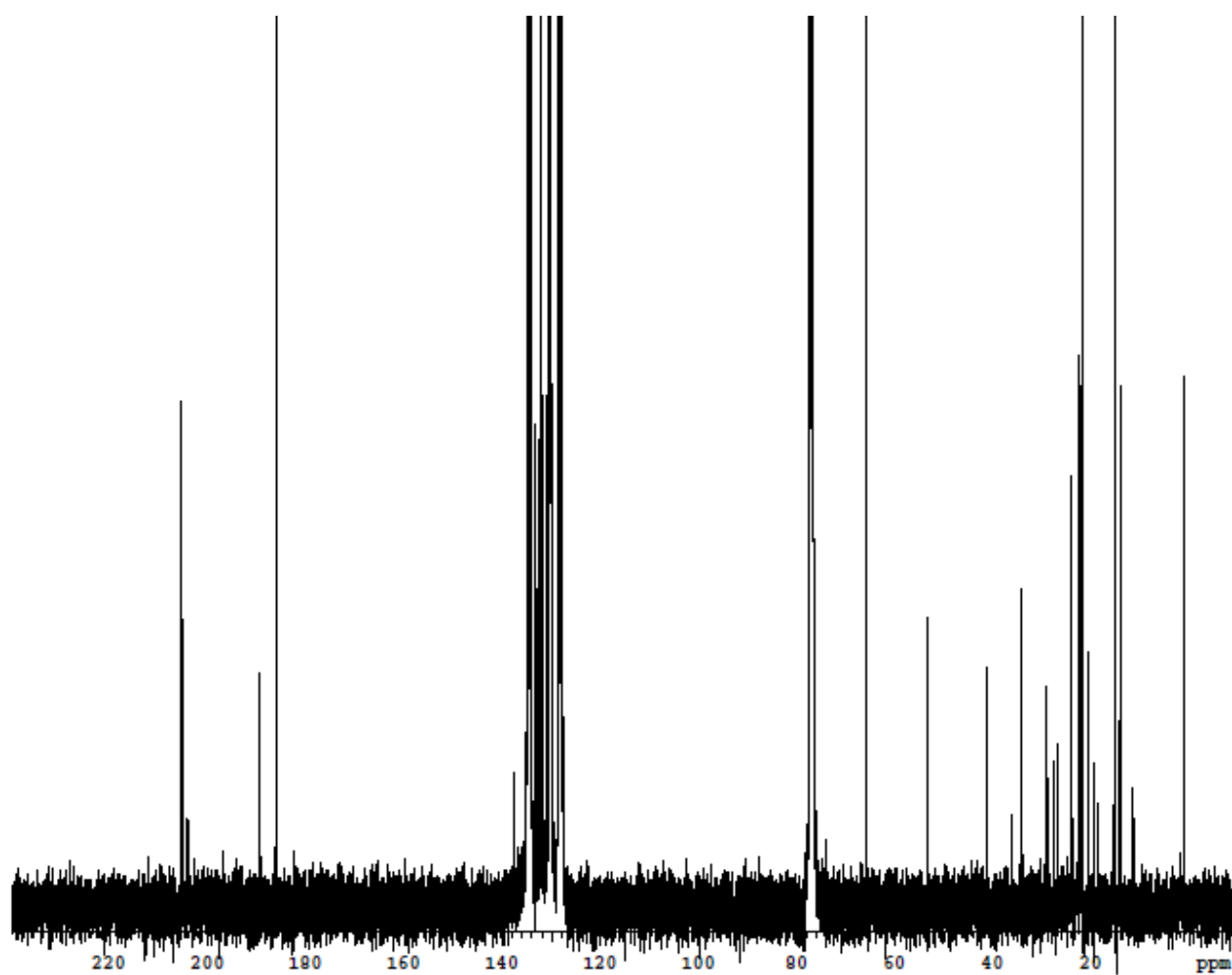


Figure S15b. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **6** species.

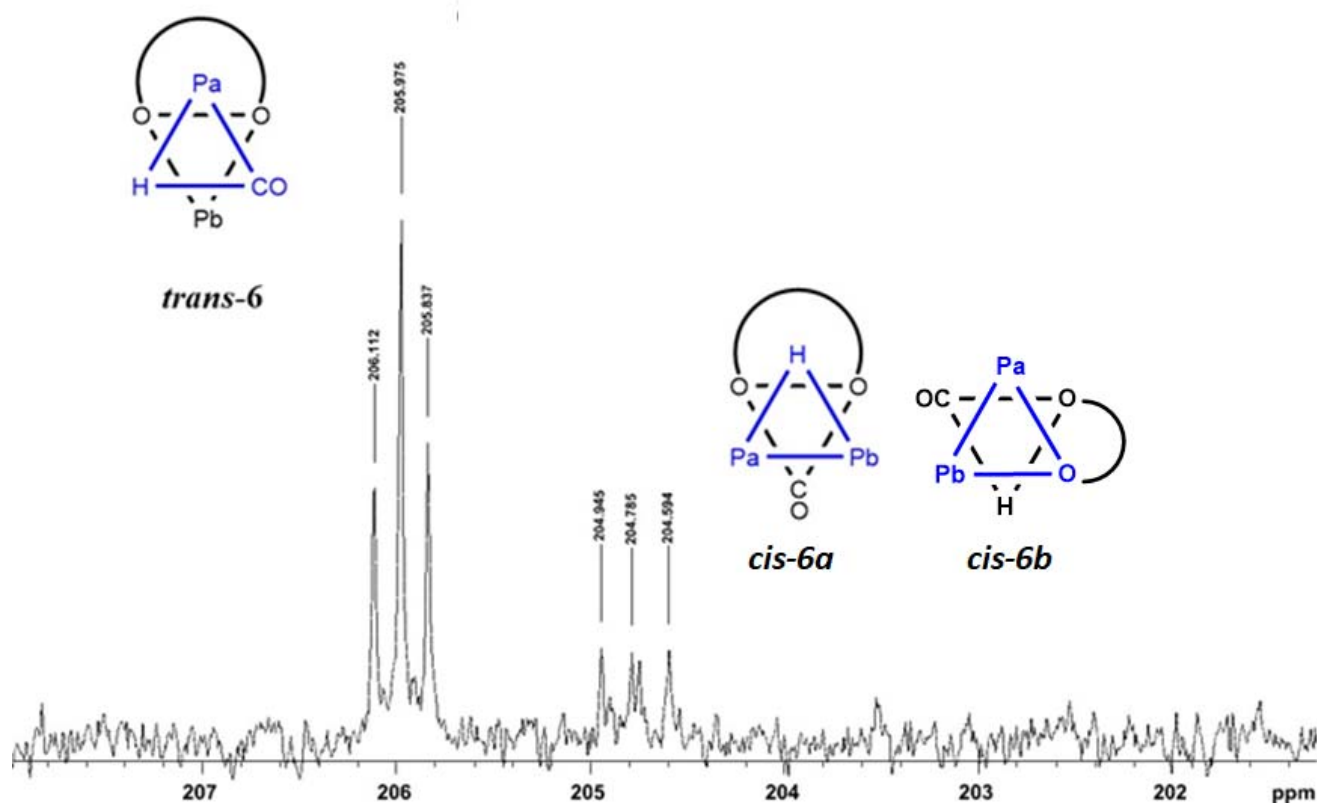


Figure S15c. $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **6** species.

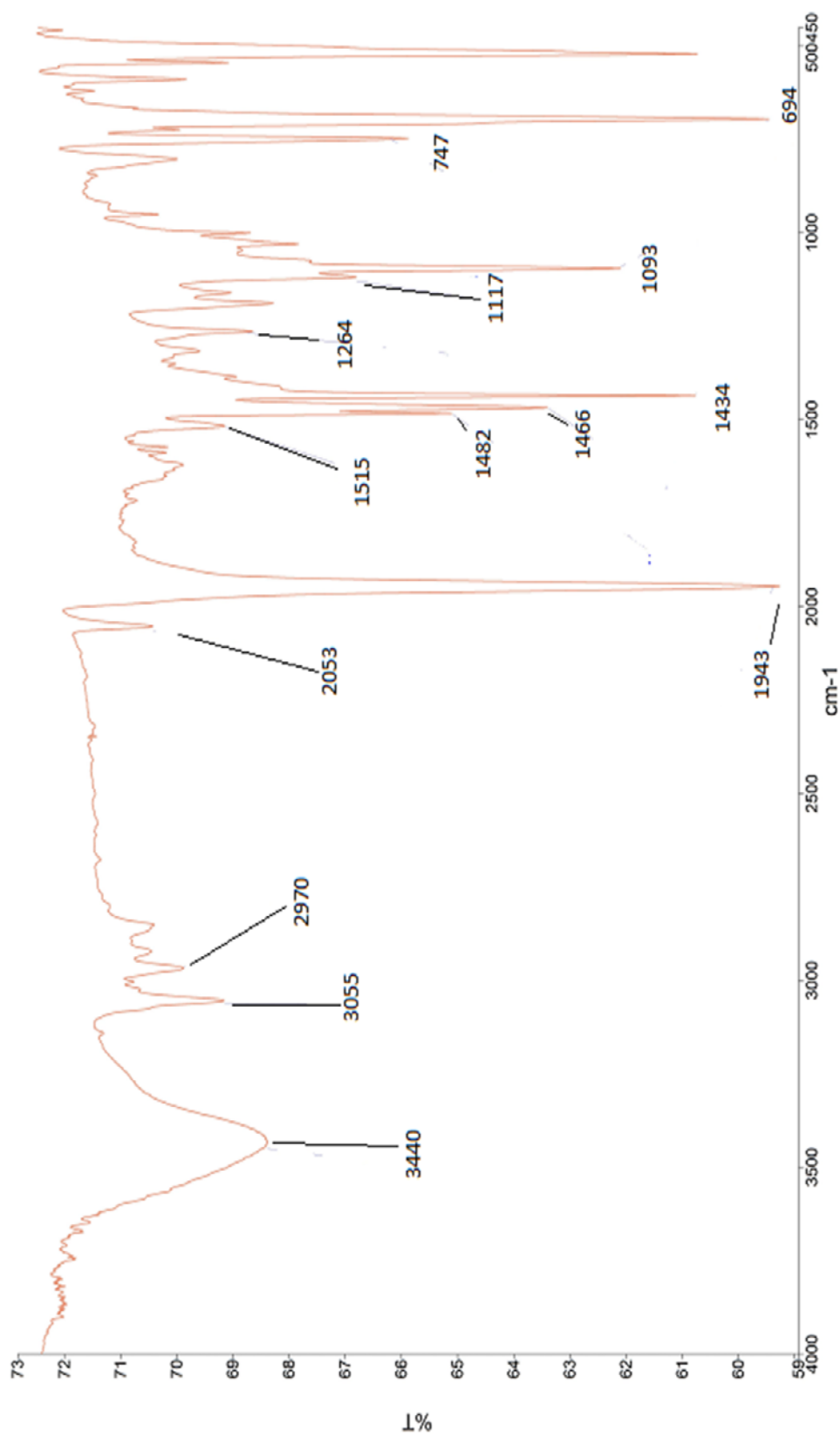


Figure S16. FT-IR (KBr) $\kappa^1(\text{O})\text{Ac}^-$, $\kappa^2(\text{O},\text{O})\text{Ac}^-[\text{Ru}(\text{CO})(\text{PPh}_3)_2]$, **7**

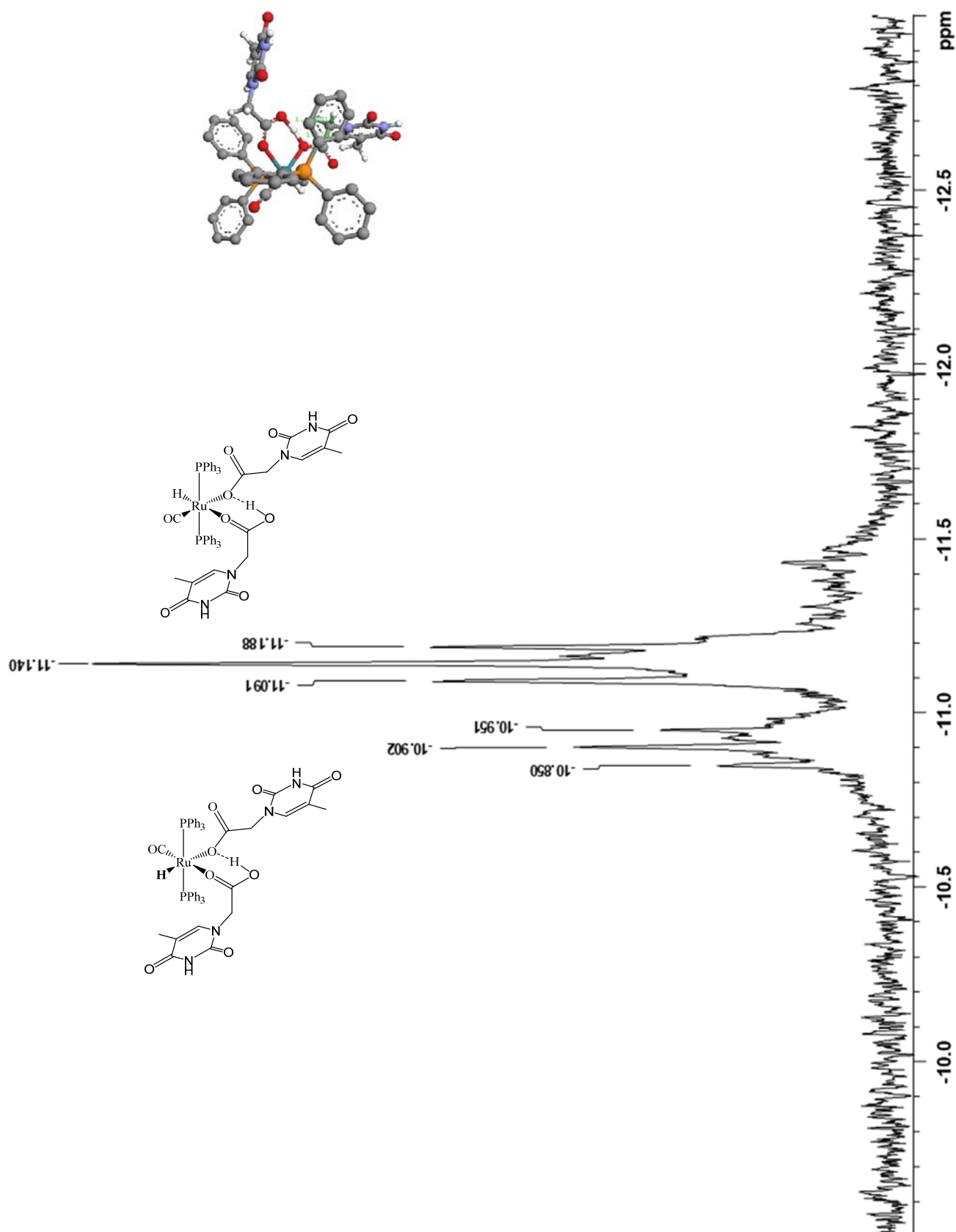


Figure S18a. Portion of hydride in ^1H -NMR spectrum in CDCl_3 of plausible intermediates of the type $\kappa^1(\text{O}), \kappa^2(\text{O})\text{-}[\text{THCH}_2\text{C}(\text{O})\text{O}\cdots\text{H}\cdots\text{OC}(\text{O})\text{CH}_2\text{TH}][\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)_2]$, **A** analogous to **B** intermediate

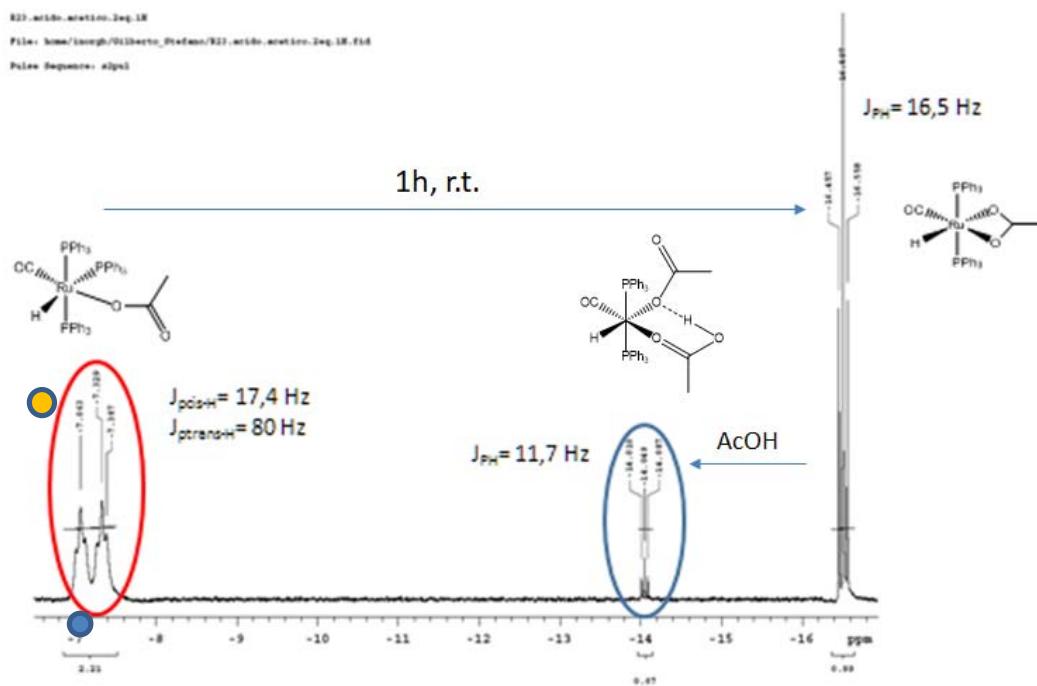


Figure S18b. Portion of hydride in ^1H -NMR spectrum in CDCl_3 of plausible intermediates of the type $\kappa^1(\text{O}), \kappa^2(\text{O})\text{-}[\text{MeC}(\text{O})\text{O}\cdots\text{H}\cdots\text{OC}(\text{O})\text{Me}][\text{Ru}(\text{CO})\text{H}(\text{PPh}_3)_2]$ **B**.

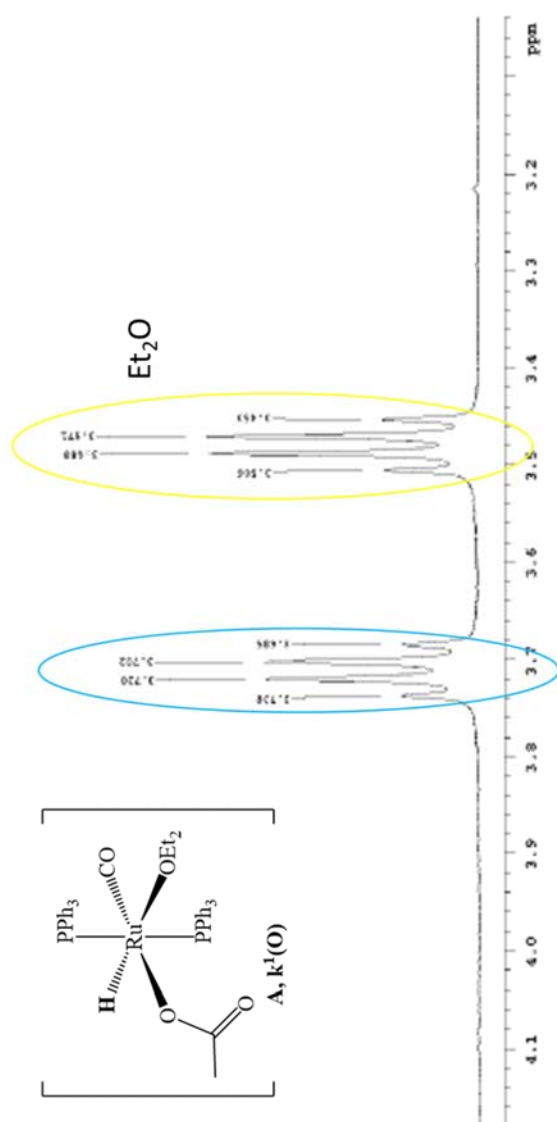


Figure S18c. ^1H -NMR portion of the spectrum of **A** in CDCl_3 displaying the CH_2 moiety of the Et_2O solvent, remarkably shifted upon Ru-coordination

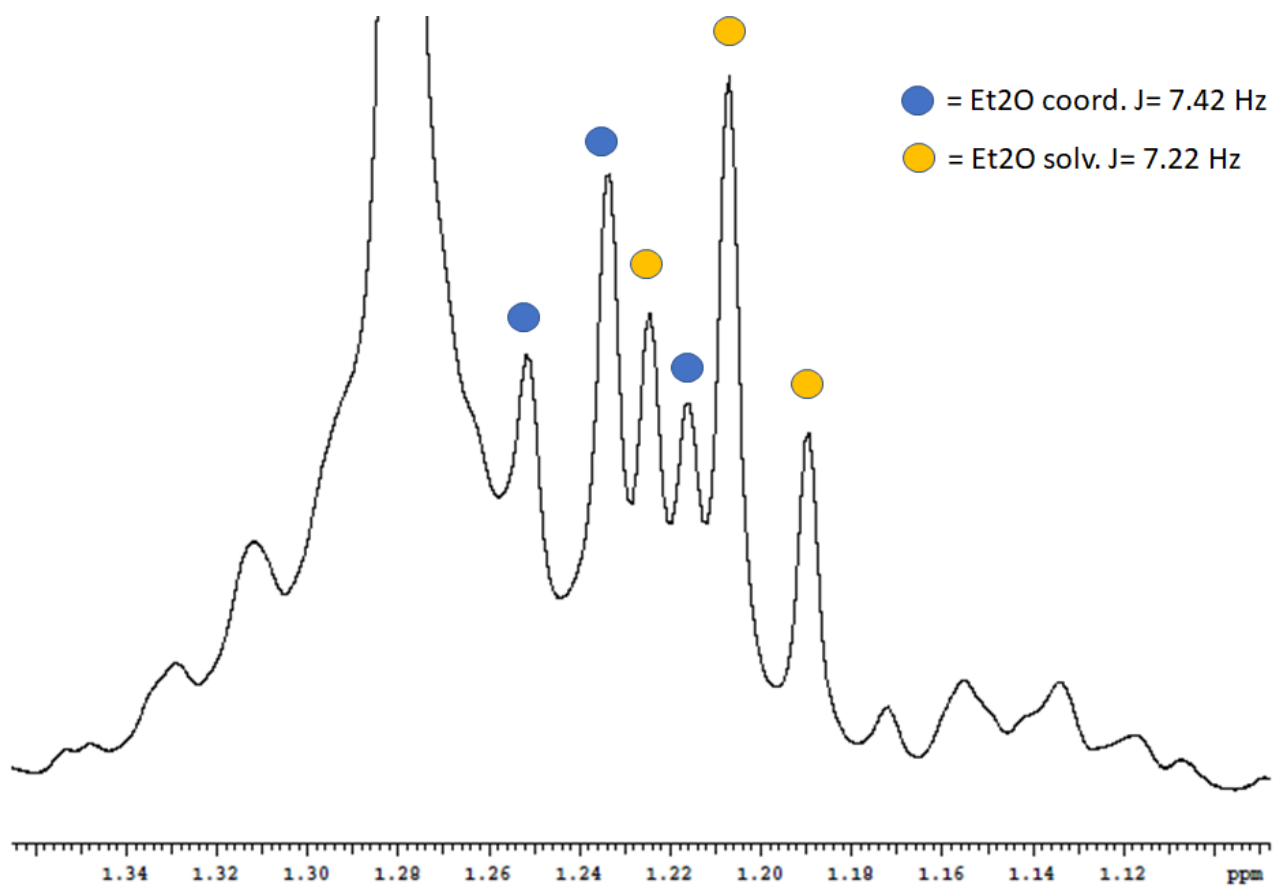


Figure S18d. ¹H-NMR portion of the spectrum of **A** in CDCl₃ displaying the CH₃ moiety of the Et₂O solvent, shifted upon Ru-coordination