Proton-responsive Ruthenium(II) Catalysts for the Solvolysis of Ammonia-Borane.

Virginia San Nacianceno,[†] María A. Garralda,[†] Jon M. Matxain,[†‡] and Zoraida Freixa*[†§]

† Faculty of Chemistry, University of the Basque Country (UPV-EHU), San Sebastián, 20018, Spain

‡ Donostia International Physics Center (DIPC), San Sebastián, 20018, Spain

§ IKERBASQUE, Basque Foundation for Science, Bilbao, 48011, Spain

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In situ NMR characterizations.

***In situ* NMR catalytic experiments.**

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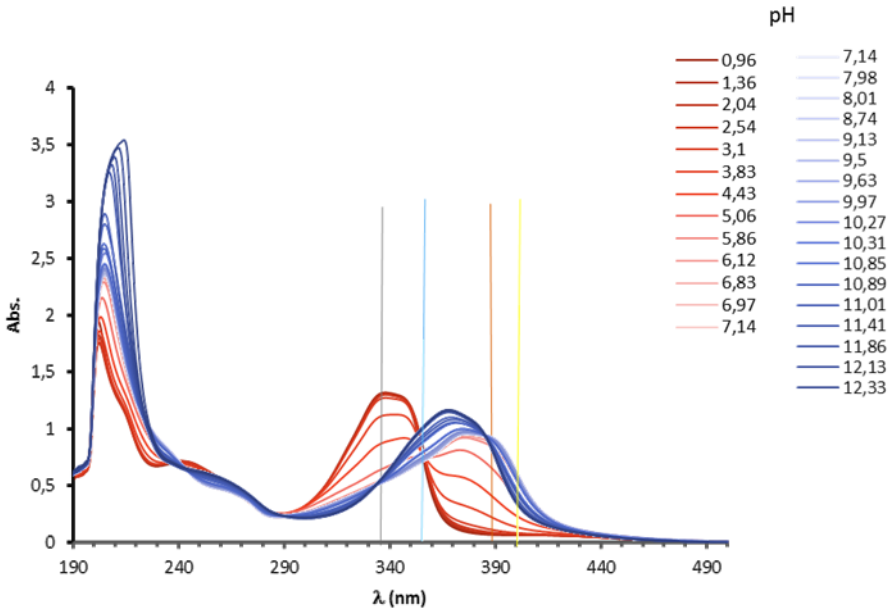
a



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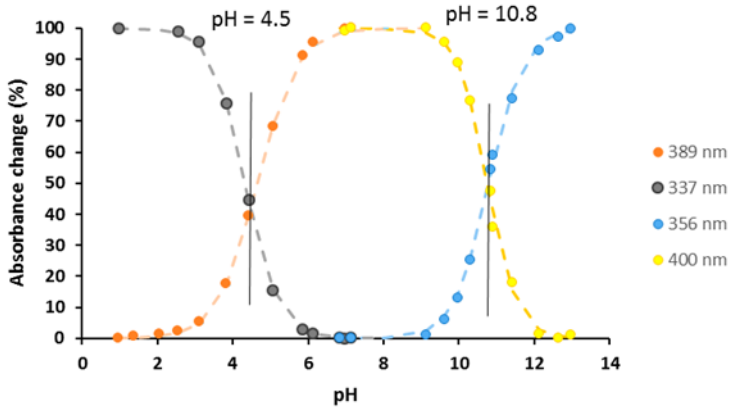
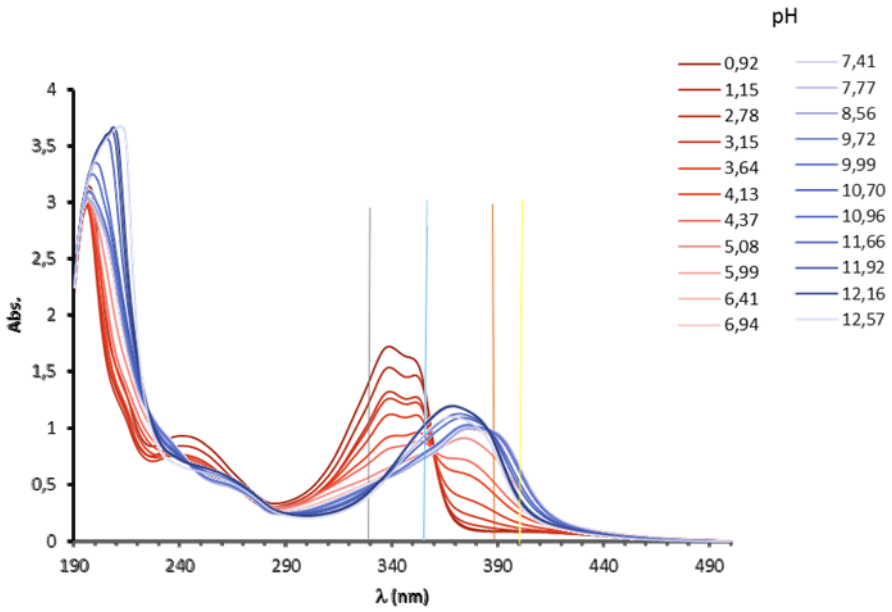


Figure S1. a) UV-vis absorption spectra of [Ru(p-Cym)(dhbp)(H_2O)](OTf)$_2$ (**2**) in a pH titration in H_2O. b) Absorbance changes at single wavelengths as a function of pH. Botzmann fits used to calculate the corresponding pH inflexion points are plotted using discontinuous lines. The pH was adjusted by mixing $0.8 \cdot 10^{-4}$ M stock solutions of complex **2** in 0.1 M HCl and 0.1 M NaOH, respectively.

a



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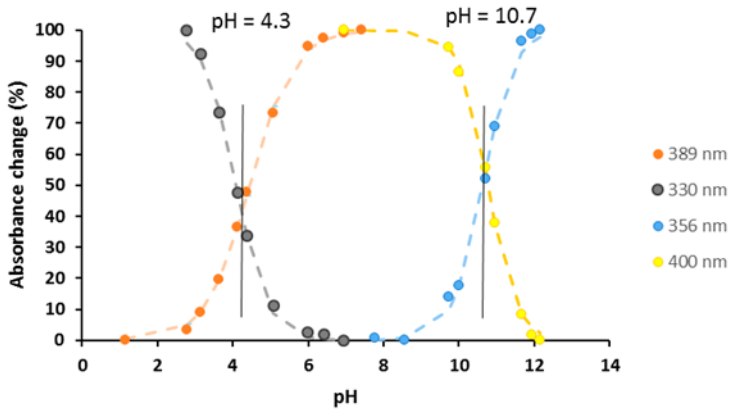
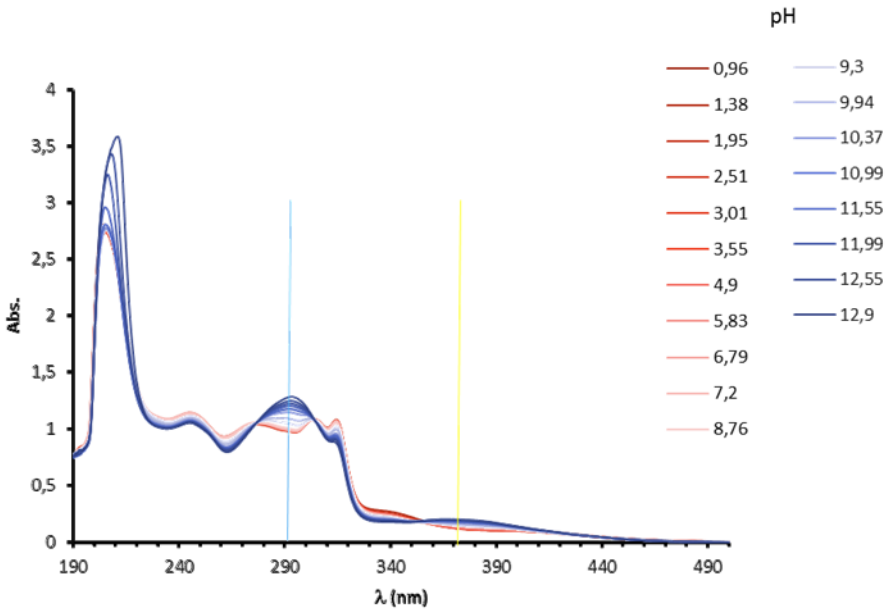


Figure S2. a) UV-vis absorption spectra of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in a pH titration in H_2O. b) Absorbance changes at single wavelengths as a function of pH. Botzmann fits used to calculate the corresponding pH inflexion points are plotted using discontinuous lines. The pH was adjusted by mixing $0.1 \cdot 10^{-3}$ M stock solutions of complex **1** in 0.02 M H_2SO_4 and 0.1 M NaOH, respectively.

a



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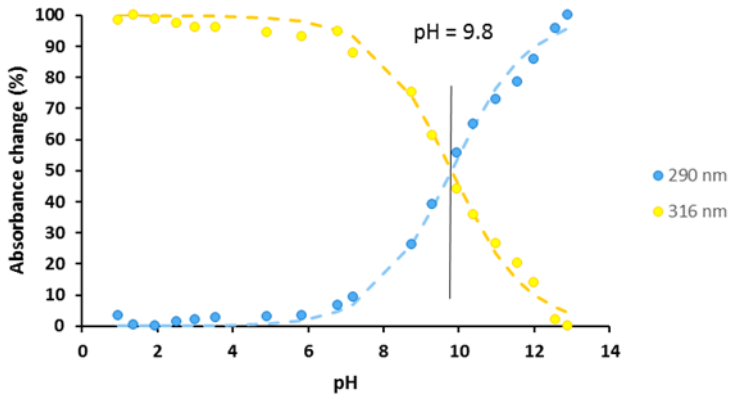


Figure S3. a) UV-vis absorption spectra of [Ru(p-Cym)(bipy)C]Cl (**V**) in a pH titration in H_2O. b) Absorbance changes at single wavelengths as a function of pH. Botzmann fits used to calculate the corresponding pH inflexion points are plotted using discontinuous lines. The pH was adjusted by mixing $0.1 \cdot 10^{-3}$ M stock solutions of complex **V** in 0.1 M HCl and 0.1 M NaOH, respectively.

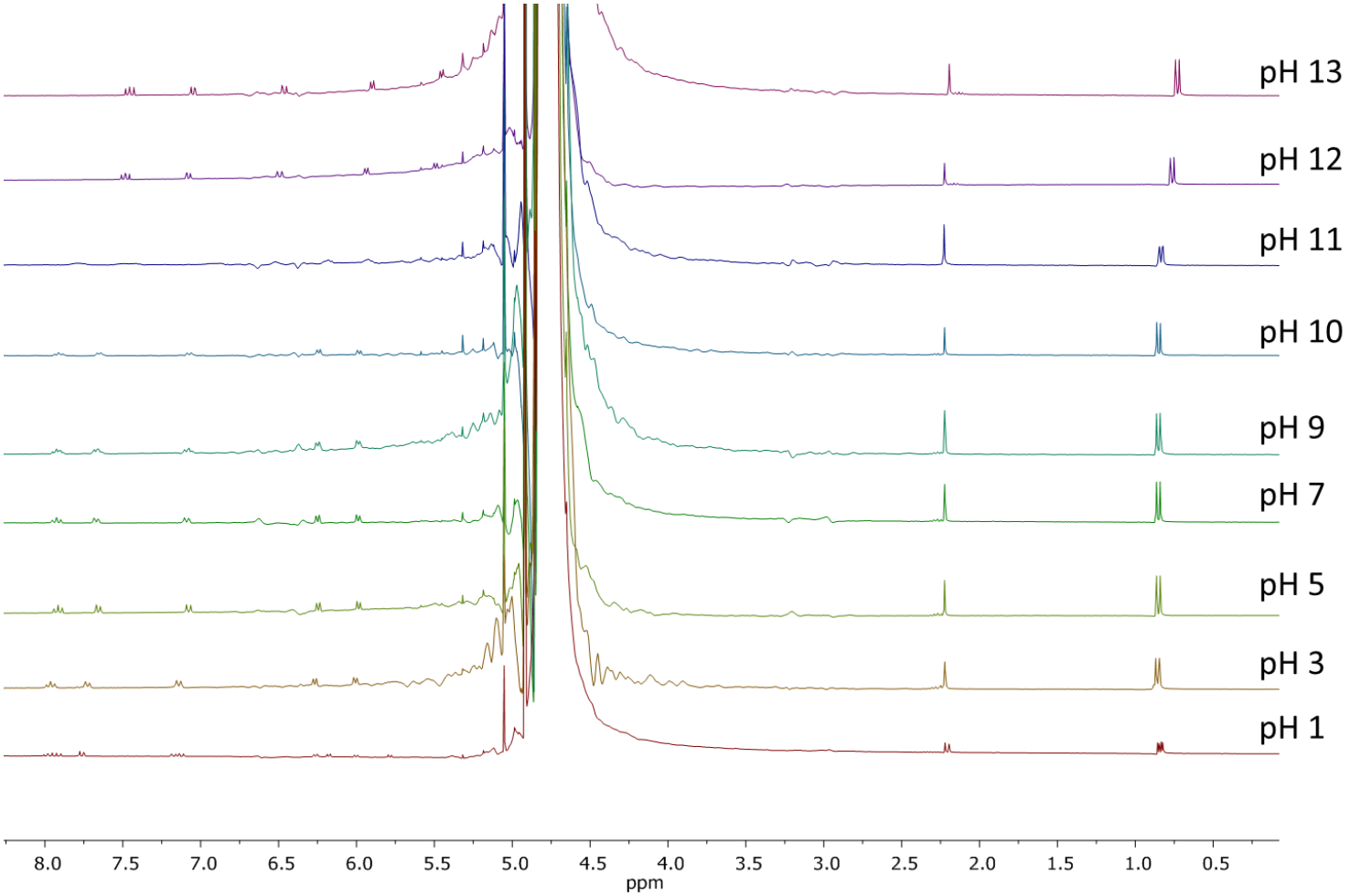


Figure S4. ^{1}H NMR spectra (300 MHz) of [Ru(p-Cym)(dhbp)(H_2O)]($OTf)_2$ (**2**) in a pH titration in H_2O (internal capillary of D_2O)**.** 0.50 mg of [Ru(p-Cym)(dhbp)(H_2O)]($OTf)_2$ (**2**) in 0.5 mL of D_2O at the indicated pH adjusted with 0.1 M stock solutions of HCl and NaOH.

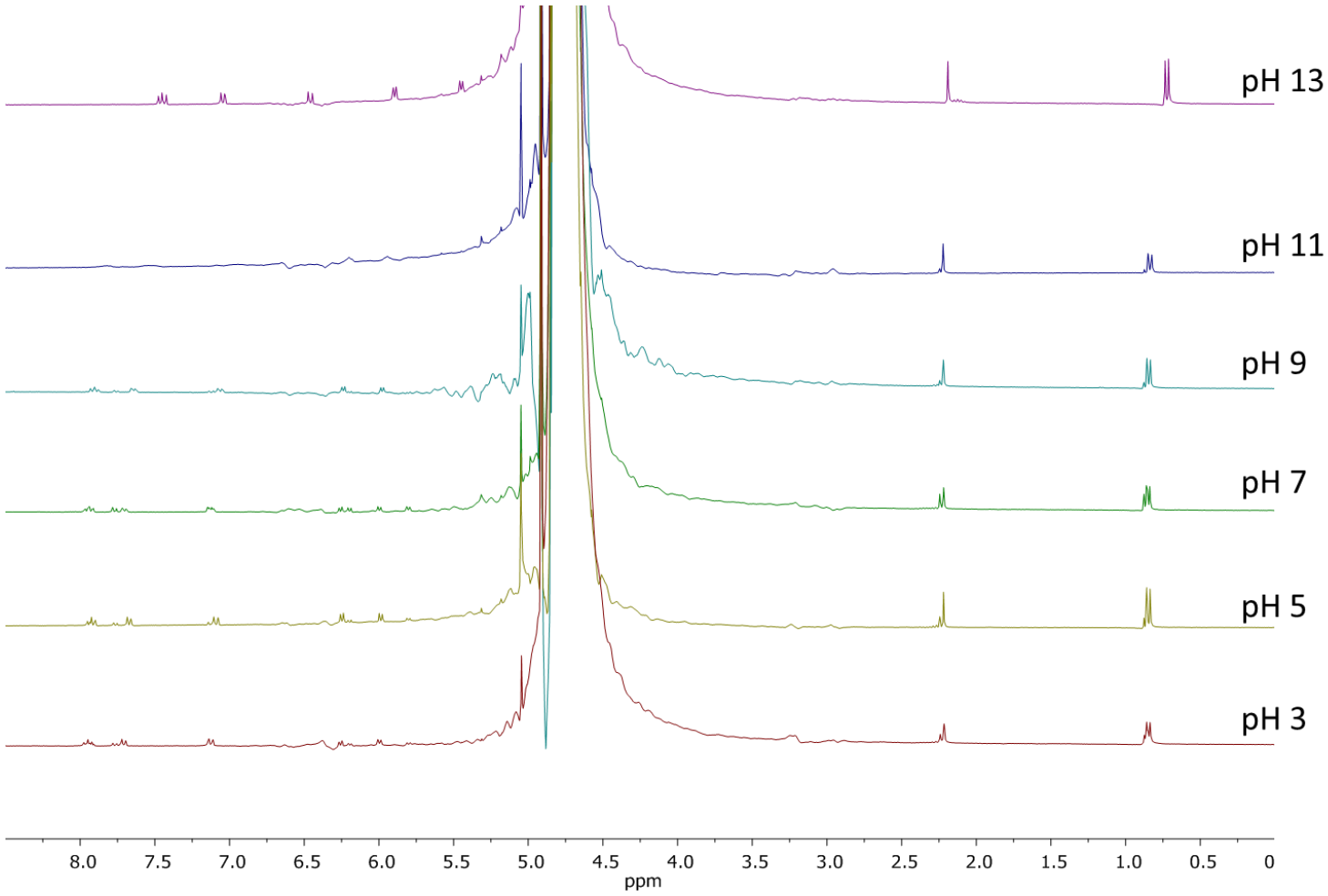


Figure S5. ^{1}H NMR spectra (300 MHz) of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in a pH titration in H_2O (internal capillary of D_2O)**.** 0.57 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O at the indicated pH adjusted with 0.1 M stock solutions of HCl and NaOH.

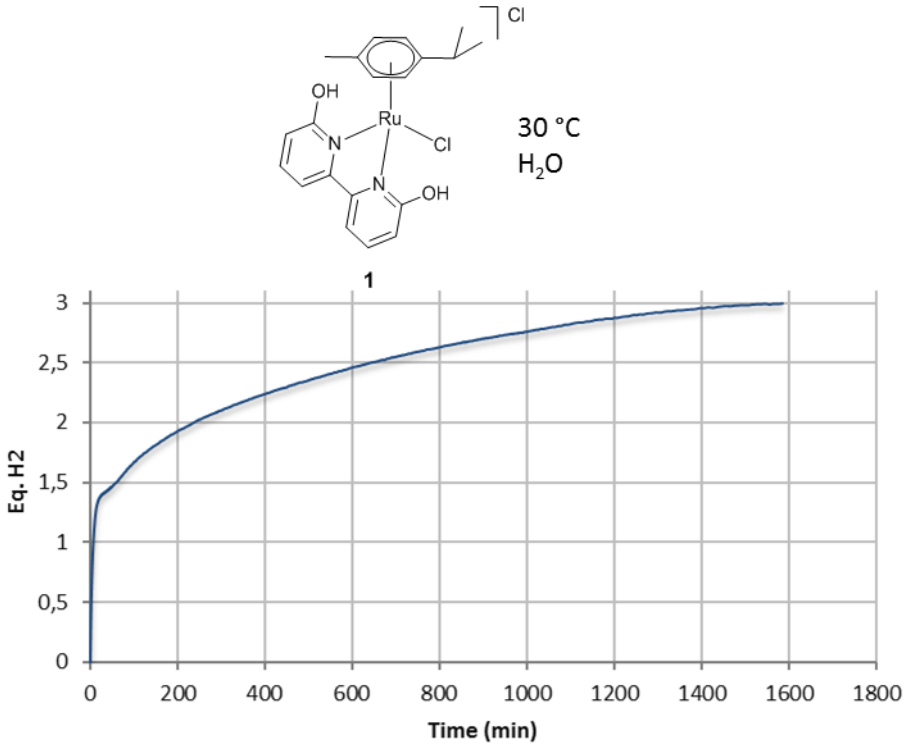


Figure S6. Reaction profile of AB hydrolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**) as precatalyst. (Table 1, Entry 1). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 30 °C.

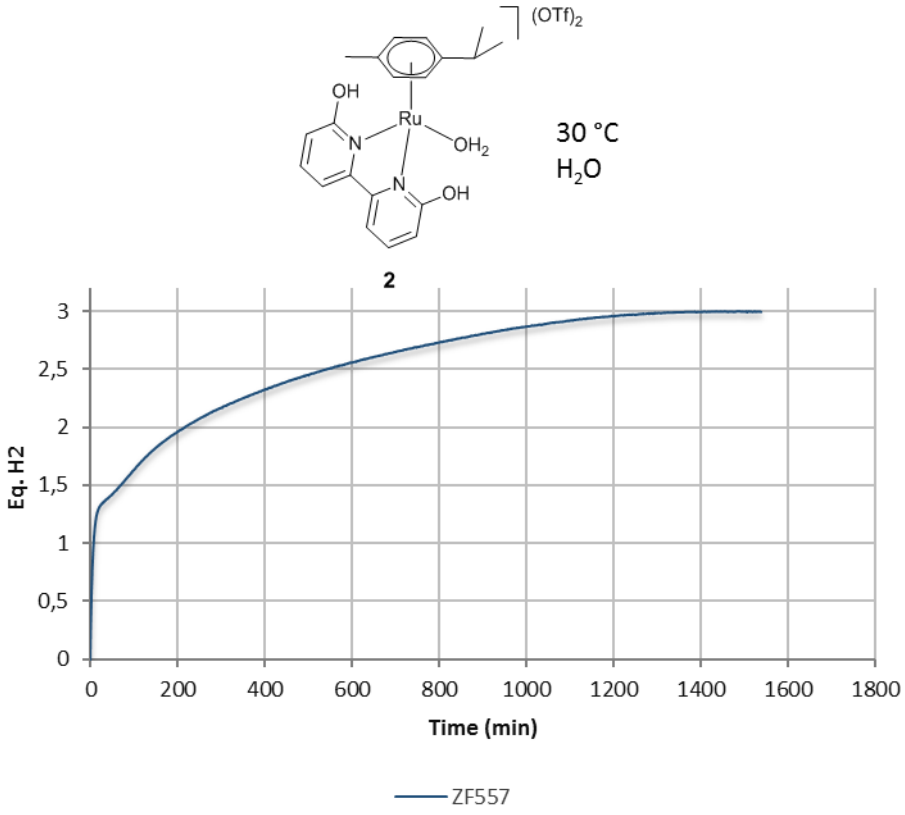


Figure S7. Reaction profile of AB hydrolysis using [Ru(p-Cym)(dhbp)(H_2O)](OTf)$_2$ (**2**) as precatalyst. (Table 1, Entry 2). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 30 °C

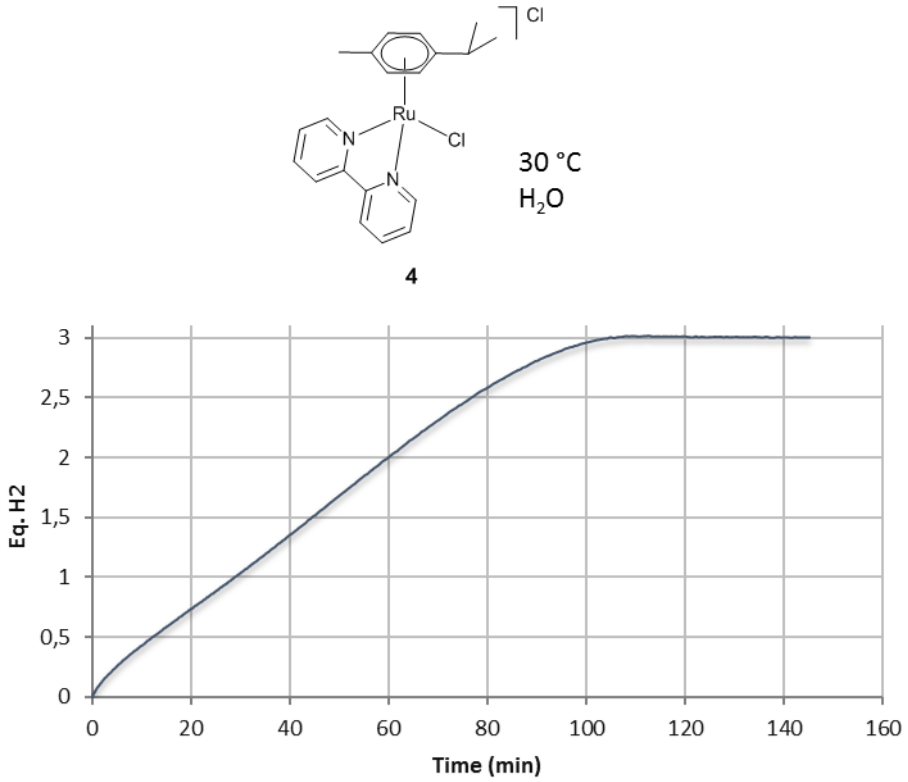


Figure S8. Reaction profile of AB hydrolysis using [Ru(p-Cym)(bipy)Cl]Cl (**V**) as precatalyst. (Table 1, Entry 3). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 30 °C.

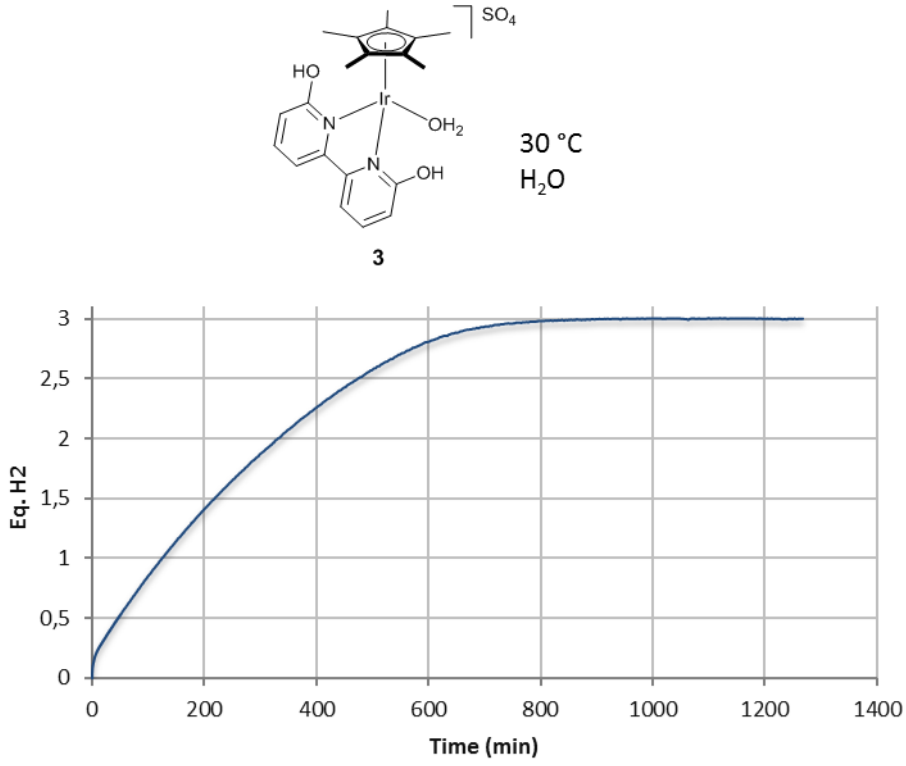


Figure S9. Reaction profile of AB hydrolysis using [IrCp*(dhbp)Cl]Cl (Himeda's catalyst) (**VI**) as precatalyst. (Table 1, Entry 4). Conditions: [Ir] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 30 °C.

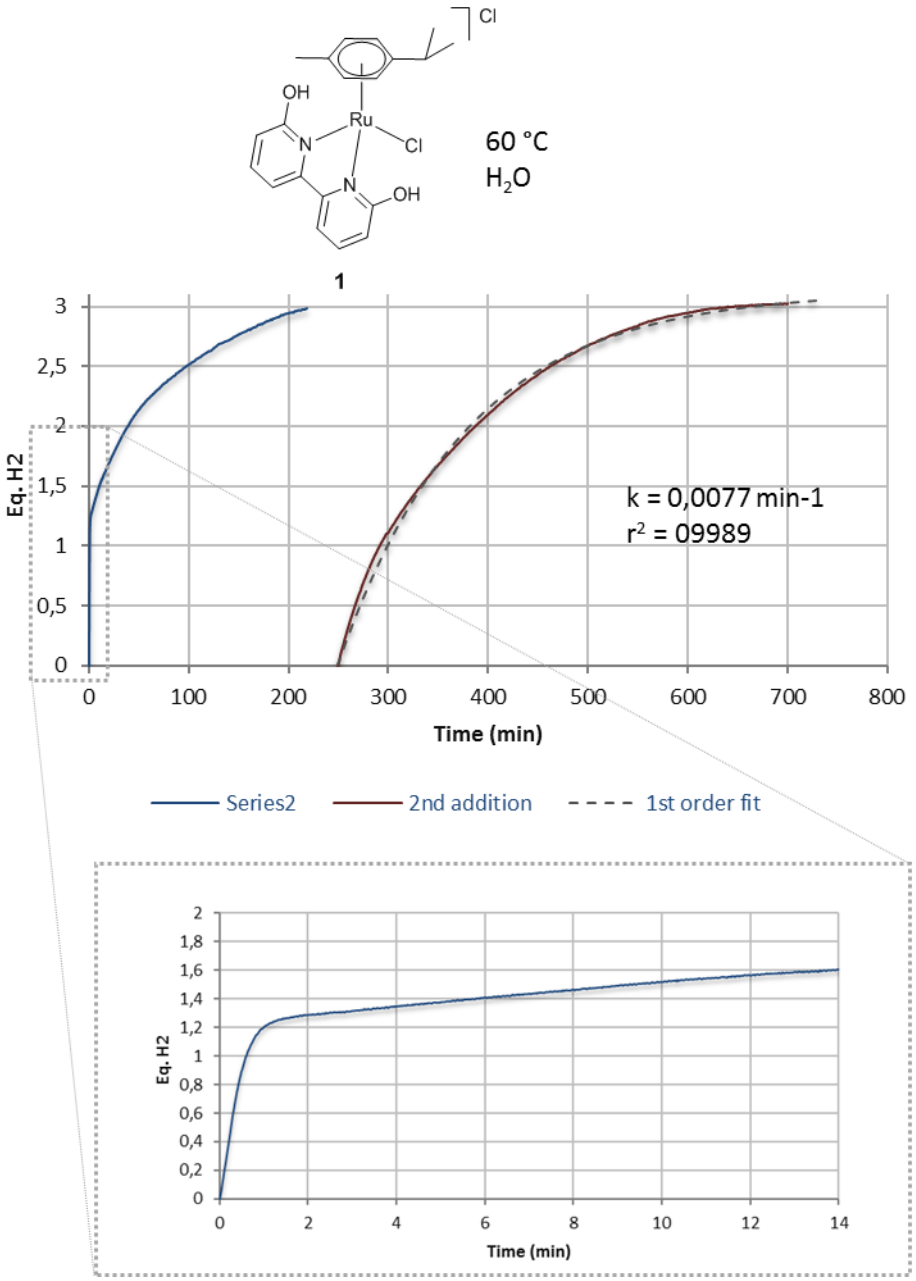


Figure S10. Reaction profiles of successive AB hydrolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**) as precatalyst. (Table 1, Entry 5). First-order kinetic adjustment for the second addition shown. Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 60 °C. Additional 21.3 mg of AB for the consecutive reaction.

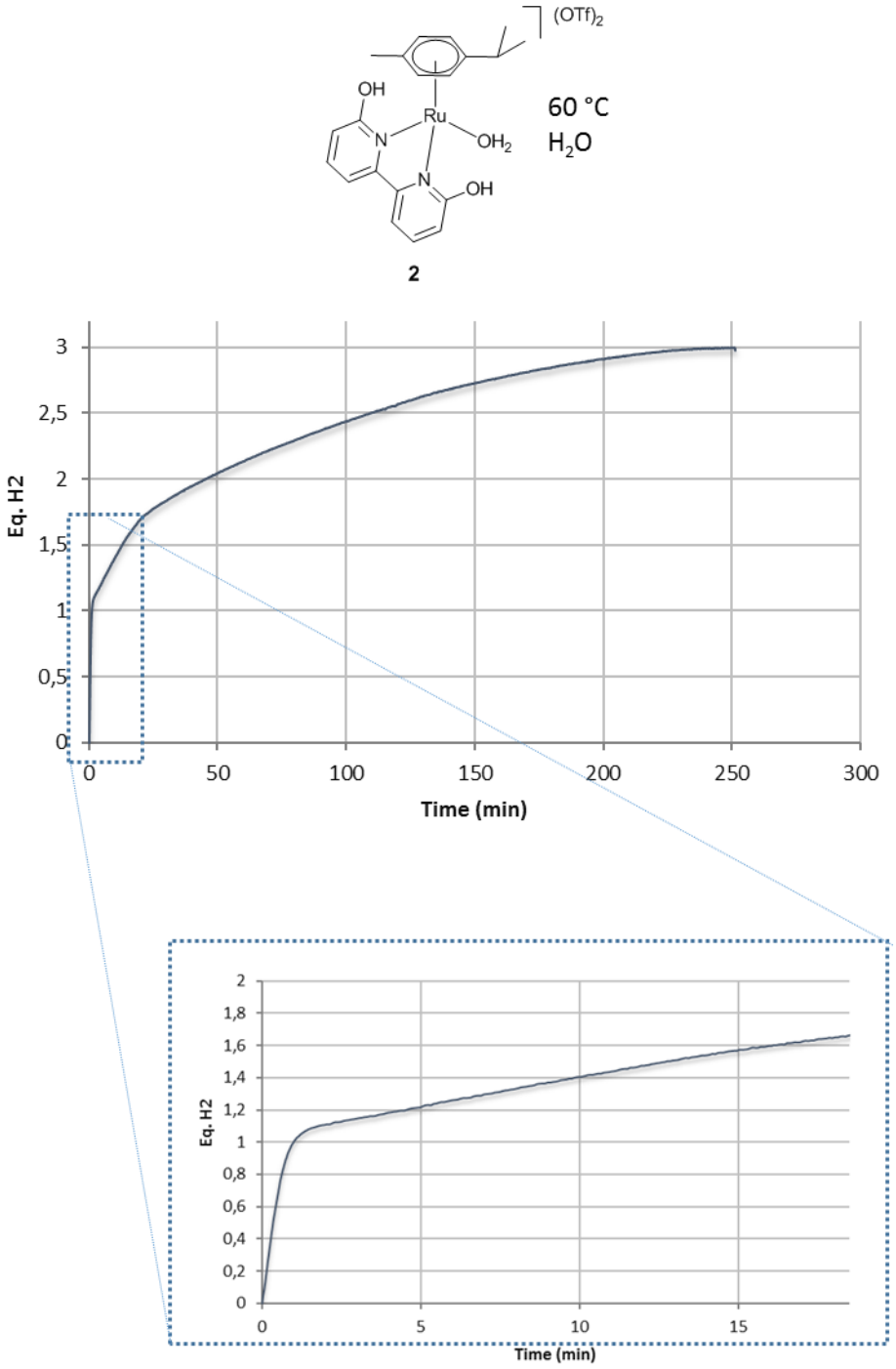


Figure S11. Reaction profile of AB hydrolysis using [Ru(p-Cym)(dhbp)(H_2O)]($OTf)_2$ (**2**) as precatalyst. (Table 1 entry 6). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 60 °C.

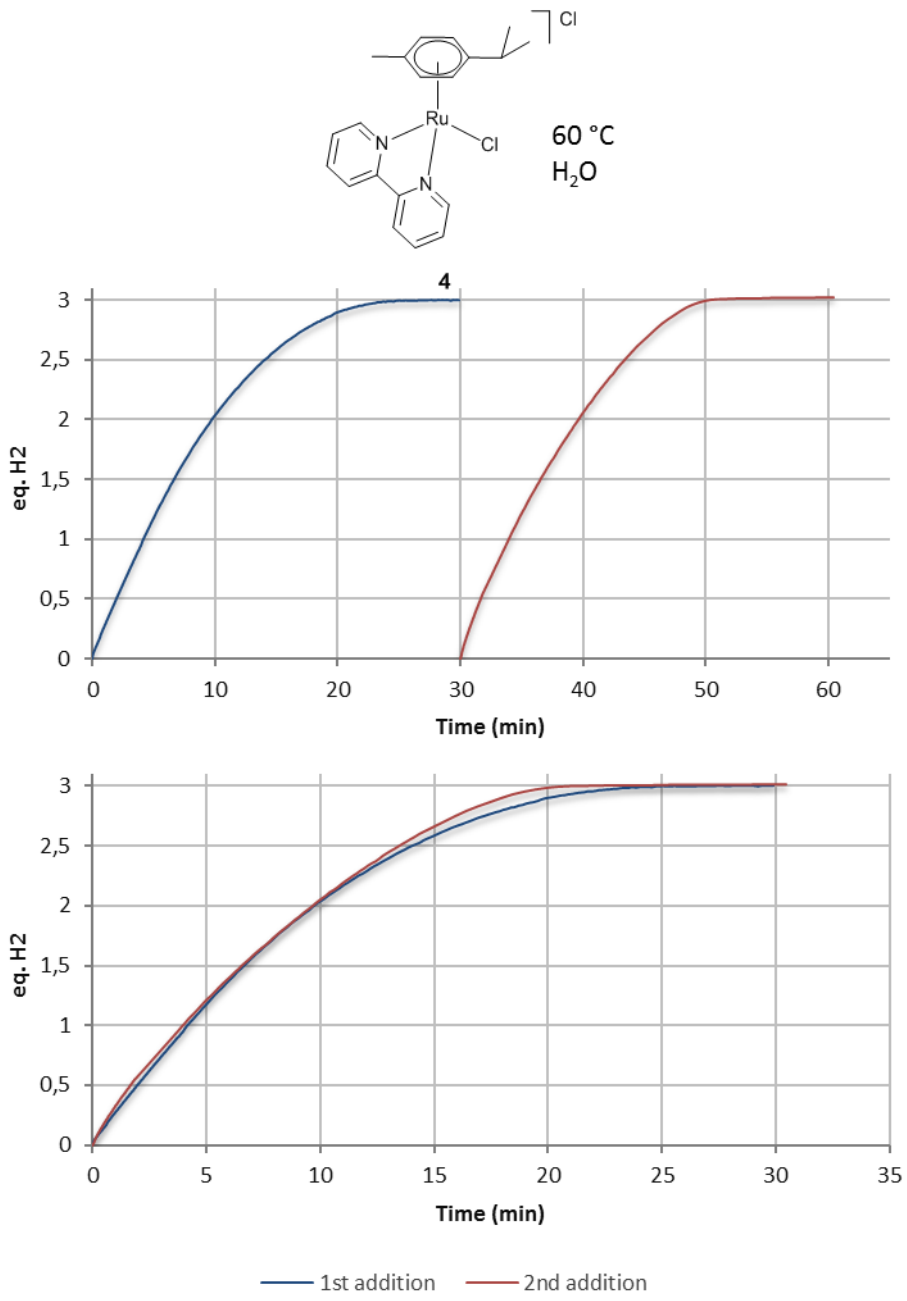


Figure S12. Reaction profiles of successive AB hydrolysis using [Ru(p-Cym)(bipy)Cl]Cl (**V**) as precatalyst. (Table 1 entry 7). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 60 °C. BOTTOM: Superimposed reaction profiles of successive reactions.

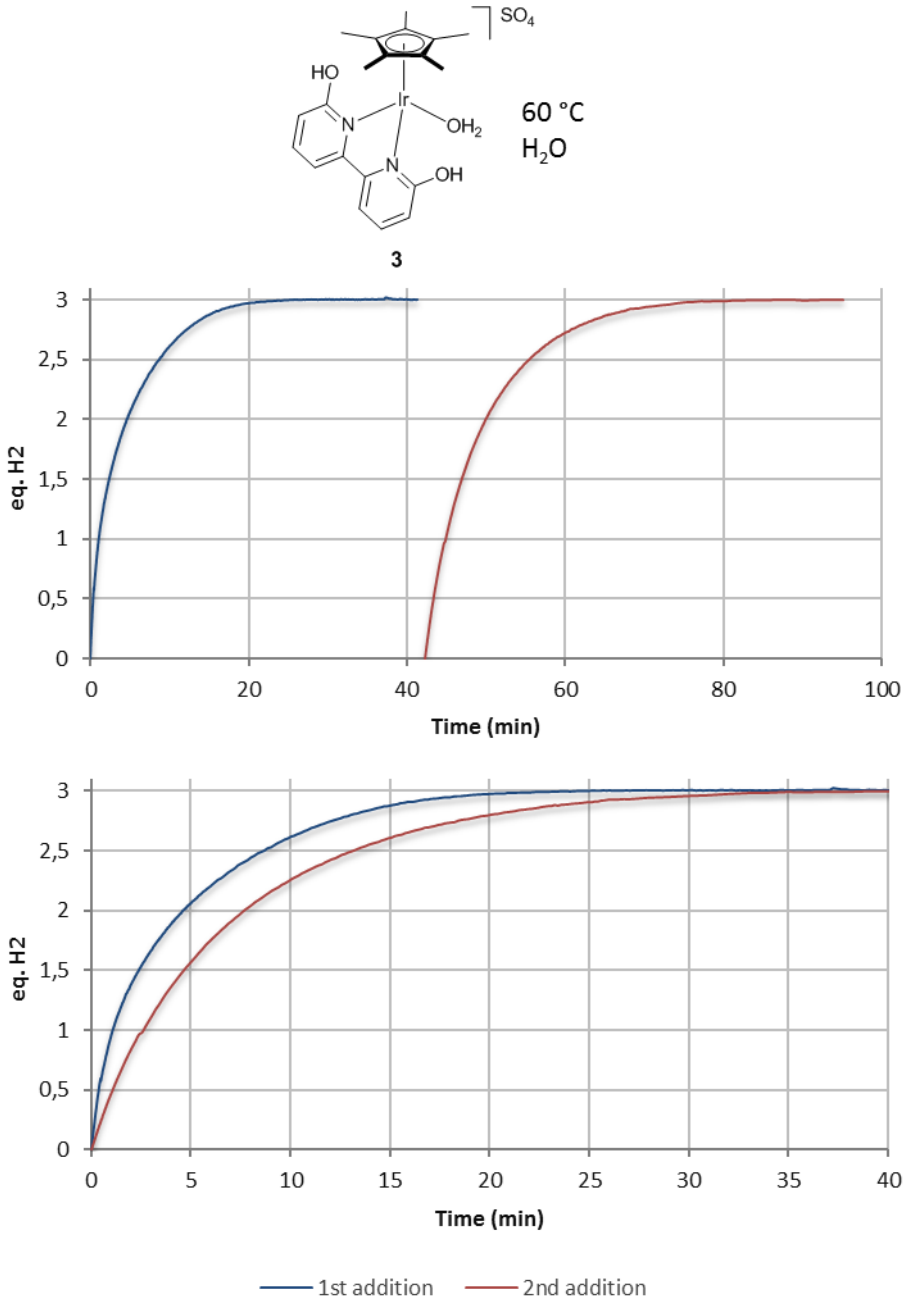


Figure S13. Reaction profiles of successive AB hydrolysis using [IrCp*(bipy-OH)(H_2O)]SO_4 (Himeda's catalyst) (**VI**). (Table 1, Entry 8). Conditions: [Ir] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Superimposed reaction profiles of successive reactions.

[Ru(pCym)(dmbp)Cl]Cl, (dmbp = 5,5'-dimethoxybipyridine) intended to be a non proton-responsive analog of compound **1** was originally synthesized and studied, for comparative purposes. The sigmoidal reaction profiles obtained, (Figures S14 and S15) together with Hg-poisoning test (Figure S16) suggested that, in this case, the catalytic activity could be partially attributed to decomposition to Ru-NPs. Further studies on the compound stability by NMR spectroscopy confirmed that it is a rather unstable compound in solution. Therefore, it has not been included in the main manuscript, but it is included here to help other researchers in further studies of related systems.

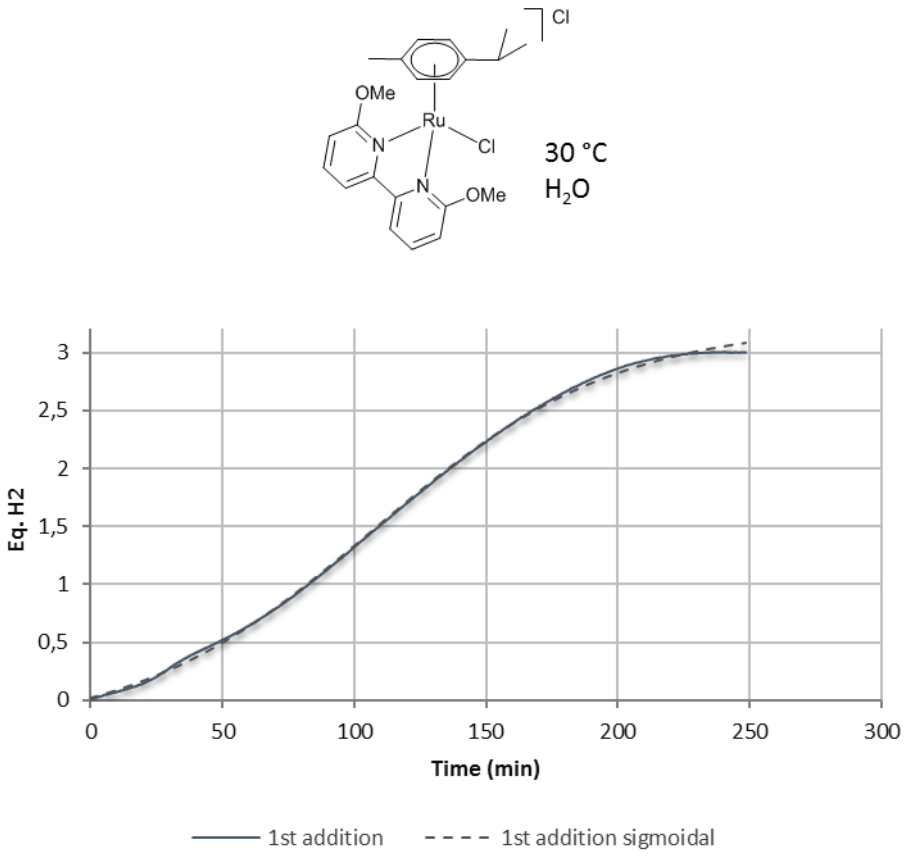


Figure S14. Reaction profile of AB hydrolysis using [Ru(p-Cym)(dmobp)Cl]Cl (dmobp = 6,6`-dimethoxybipyridine) as precatalyst. Sigmoidal fitting shown. (not discussed in manusctipt). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 30 °C.

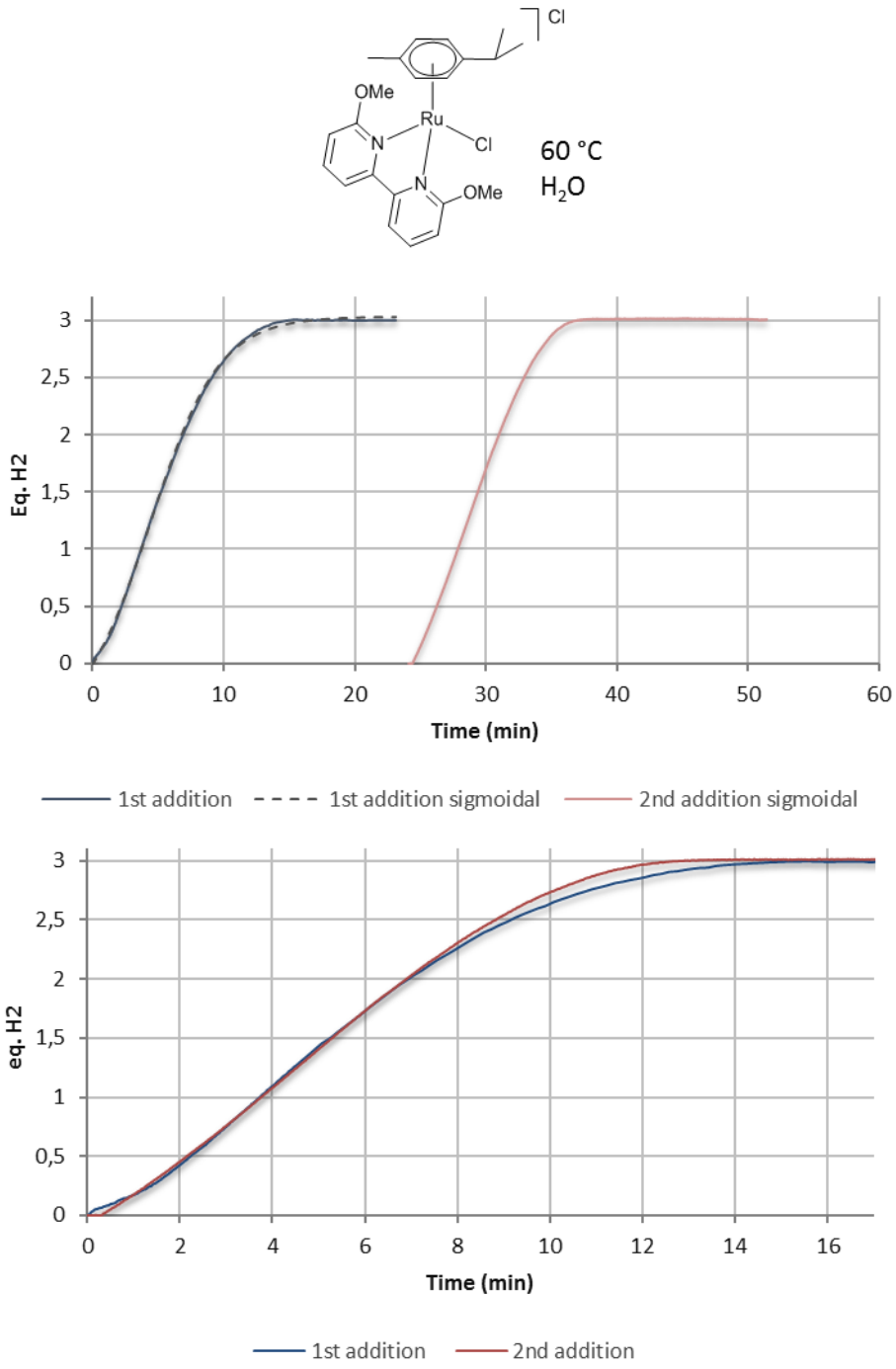


Figure S15. Reaction profiles of successive AB hydrolysis using [Ru(p-Cym)(dmobp)Cl]Cl as precatalyst. (not discussed in manuscript). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 60 °C. Additional 21.3 mg of AB for the consecutive reaction. TOP: Consecutive profiles. Sigmoidal fitting shown for the first addition. BOTTOM: Superimposed profiles (no induction period observed in the second addition).

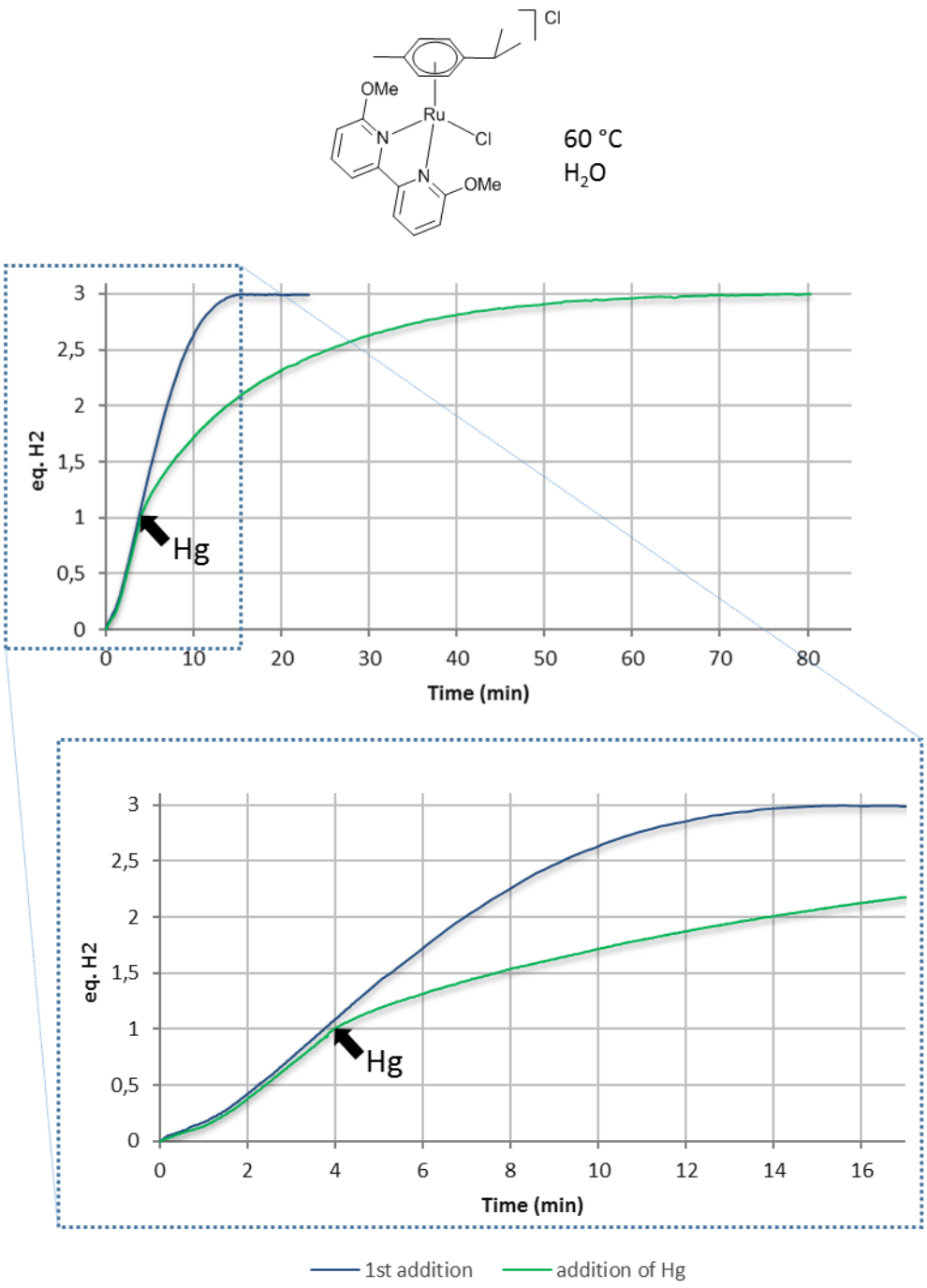


Figure S16. Reaction profiles of AB hydrolysis using [Ru(p-Cym)(dmobp)Cl]Cl as precatalyst. (not discussed in manuscript). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 60 °C. A reaction profile of a run in which Hg (1000 eq. per Ru) was added after liberation of 1 eq. of H_2 has been superimposed.

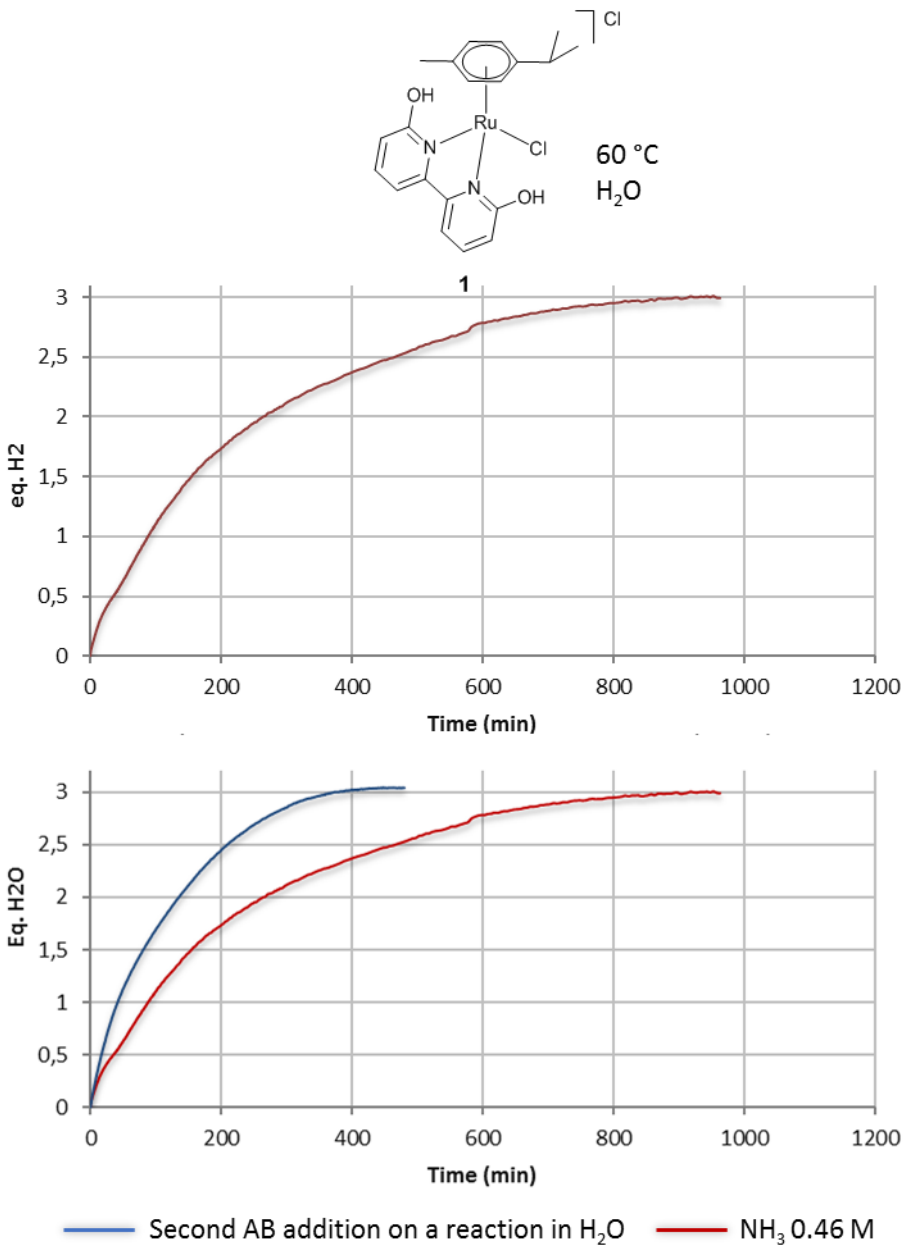


Figure S17. Reaction profiles of top: AB hydrolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**) as precatalyst. (Table 2, Entry 1). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL of a NH_3 solution 0.46 M in H_2O, 60 °C. BOTTOM: Comparison of the reaction profile after a second addition of AB on a hydrolysis reaction using catalyst **1** in H_2O ([Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 of H_2O, 60 °C, blue line), and the reaction profile in presence of NH_3 (red line).

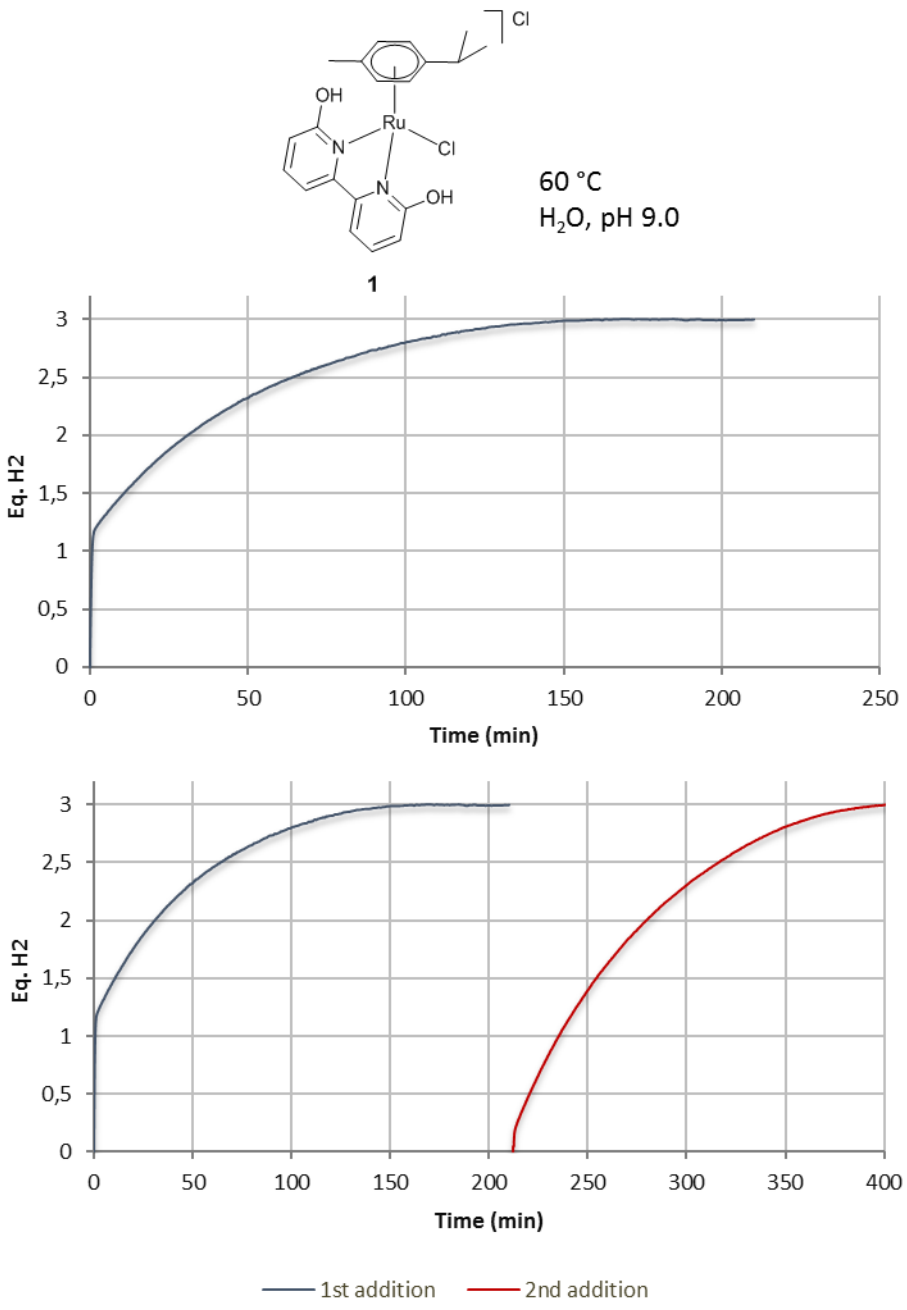


Figure S18. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 2). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL NaOH/H_2O (pH = 9.0), 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

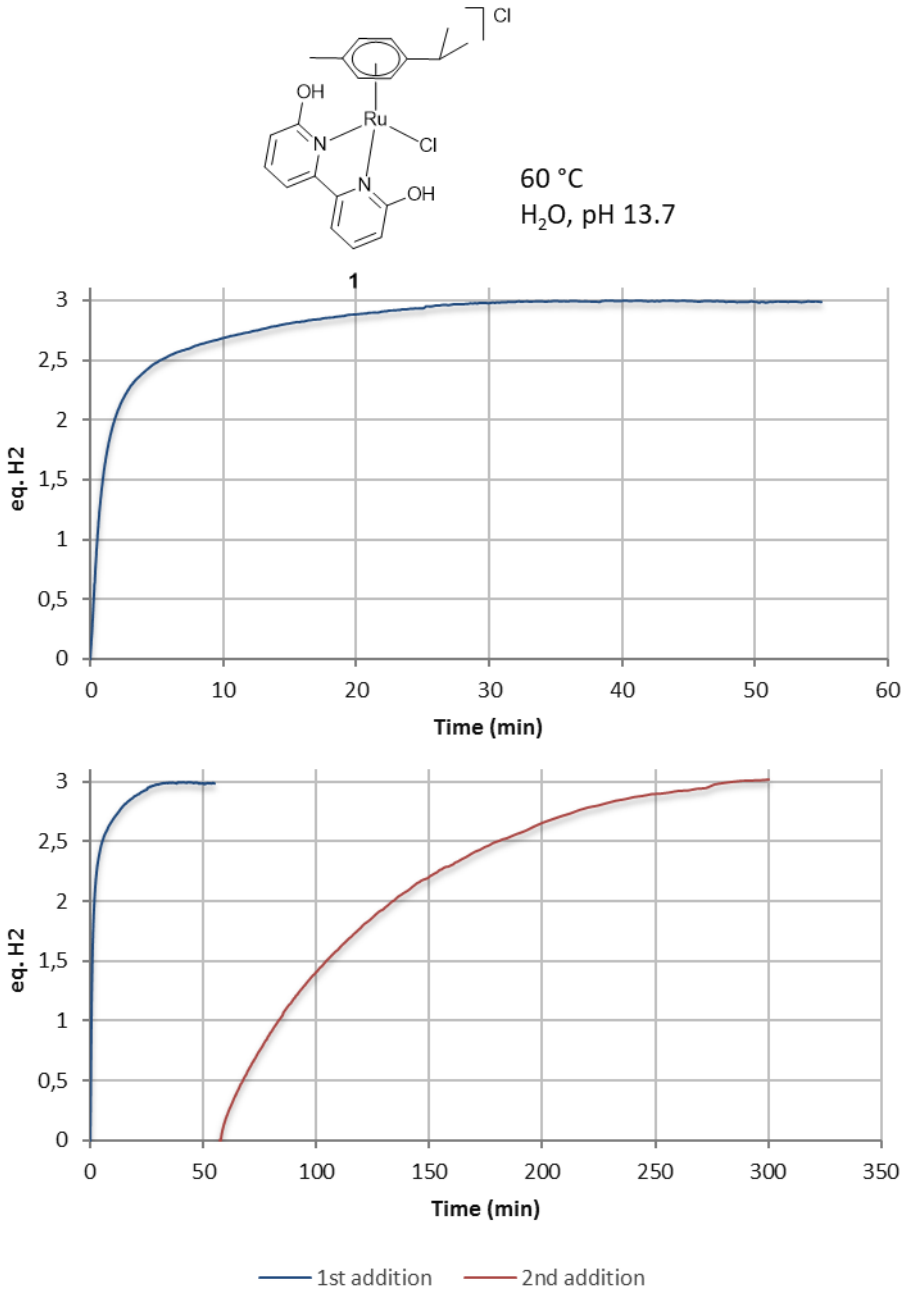


Figure S19. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 3). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL NaOH/H_2O 0.46M (pH = 13.7), 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

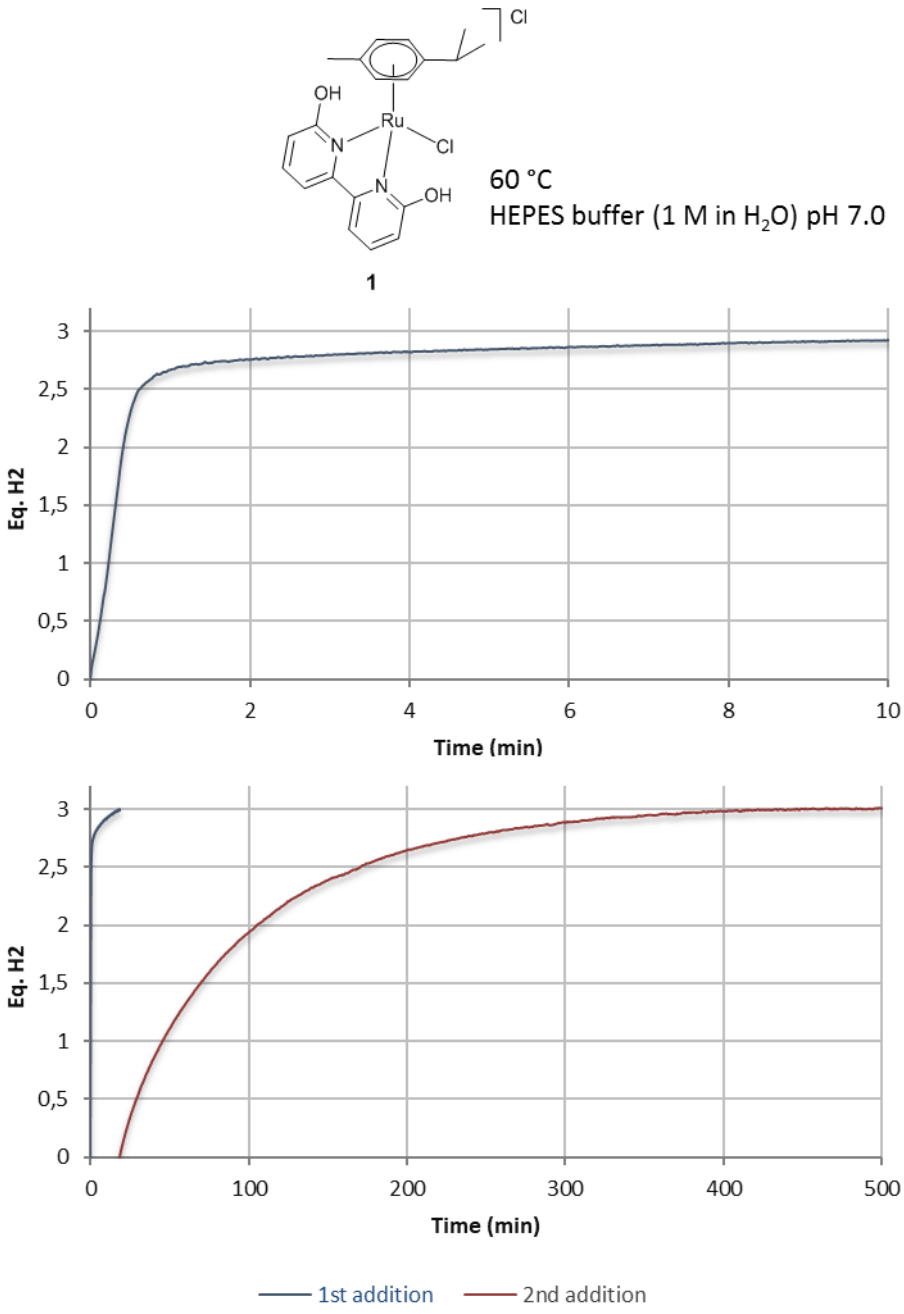


Figure S20. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 4). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL (HEPES buffer 1 M in H_2O, pH 7.0), 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

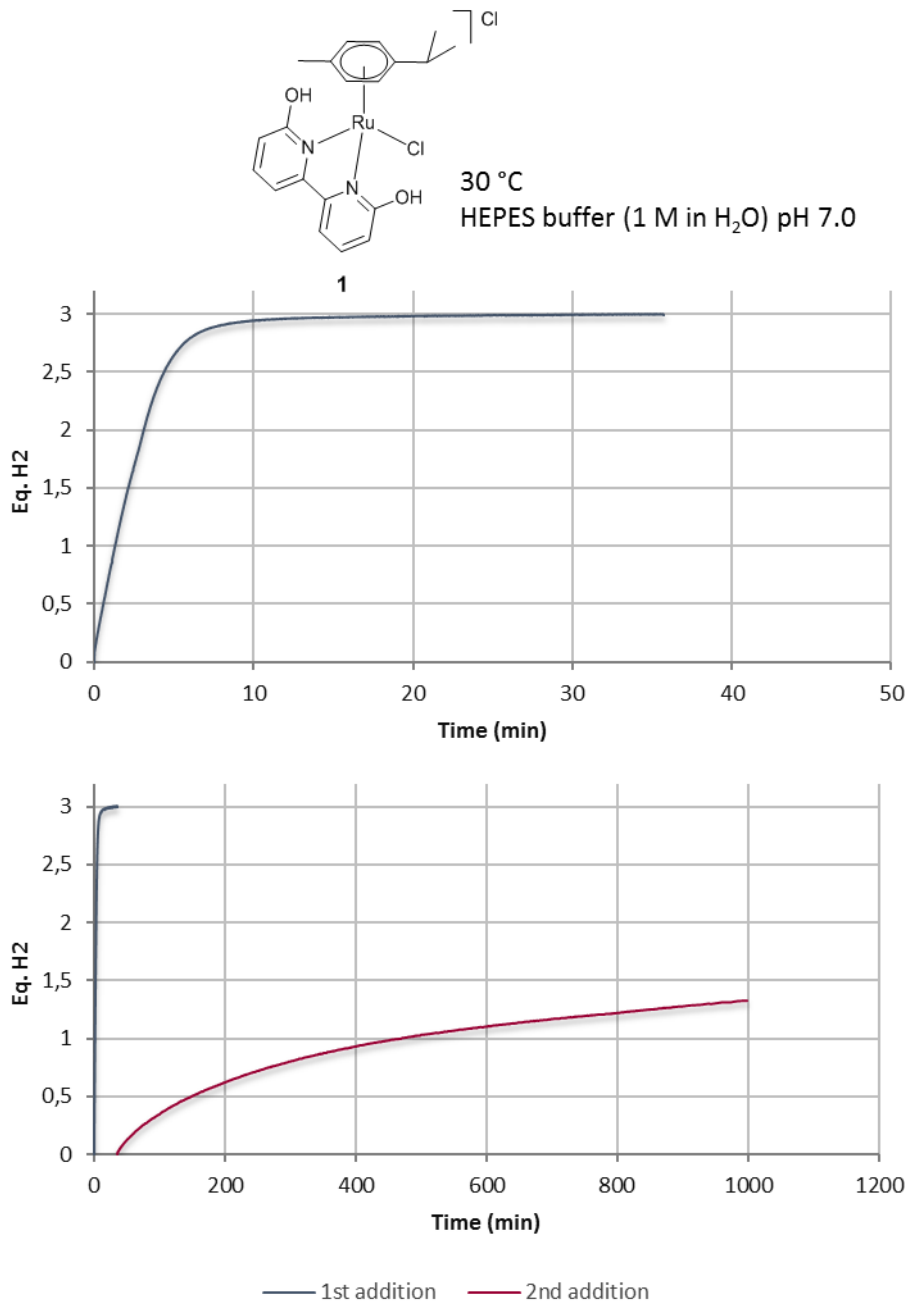


Figure S21. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 5). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL (HEPES buffer 1 M in H_2O, pH 7.0), 30 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

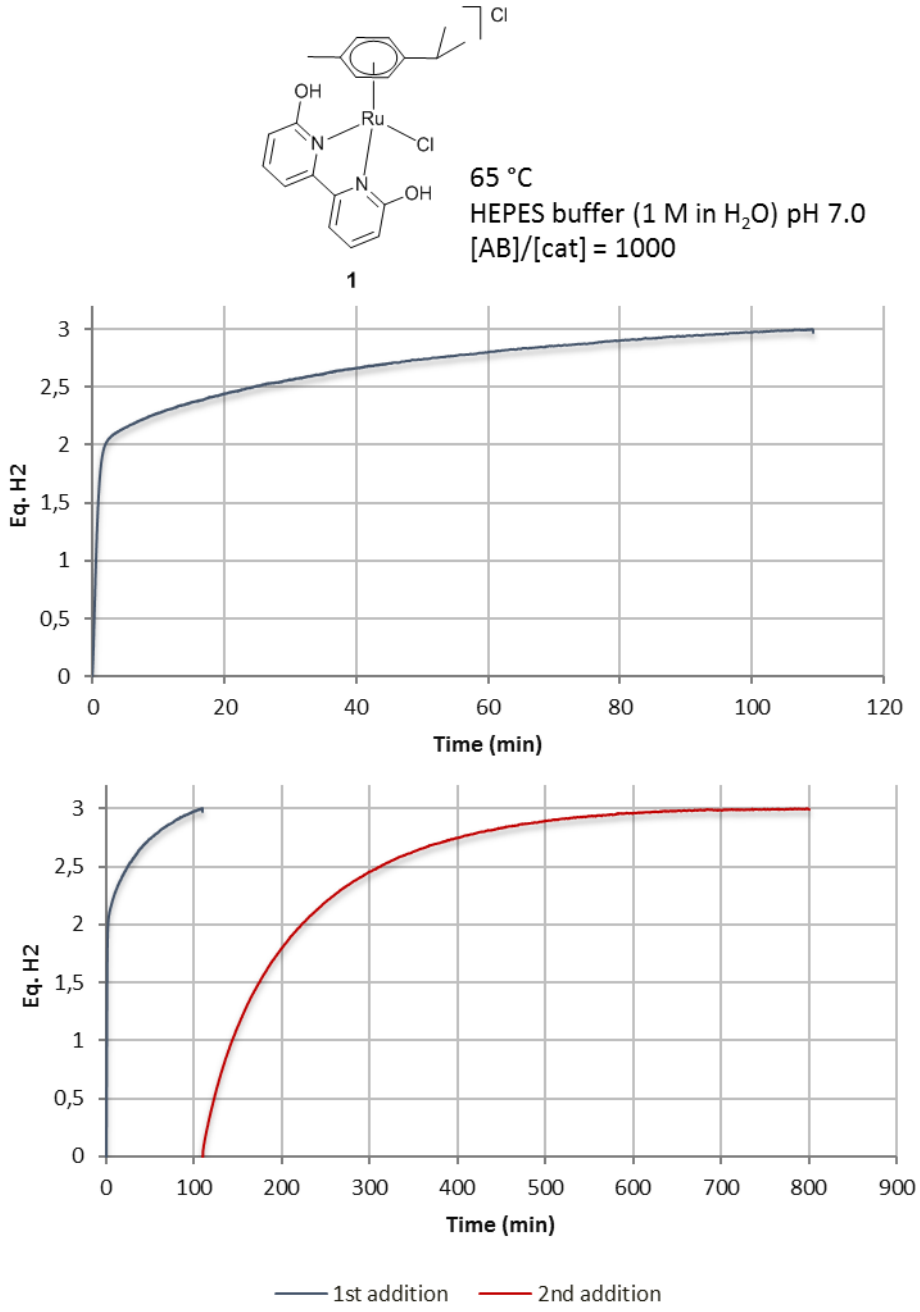


Figure S22. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 6). Conditions: [Ru] = 0.1 mM, [AB] = 0.1 M, 5 mL (HEPES buffer 1 M in H_2O, pH 7.0), 65 °C. Additional 15.4 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

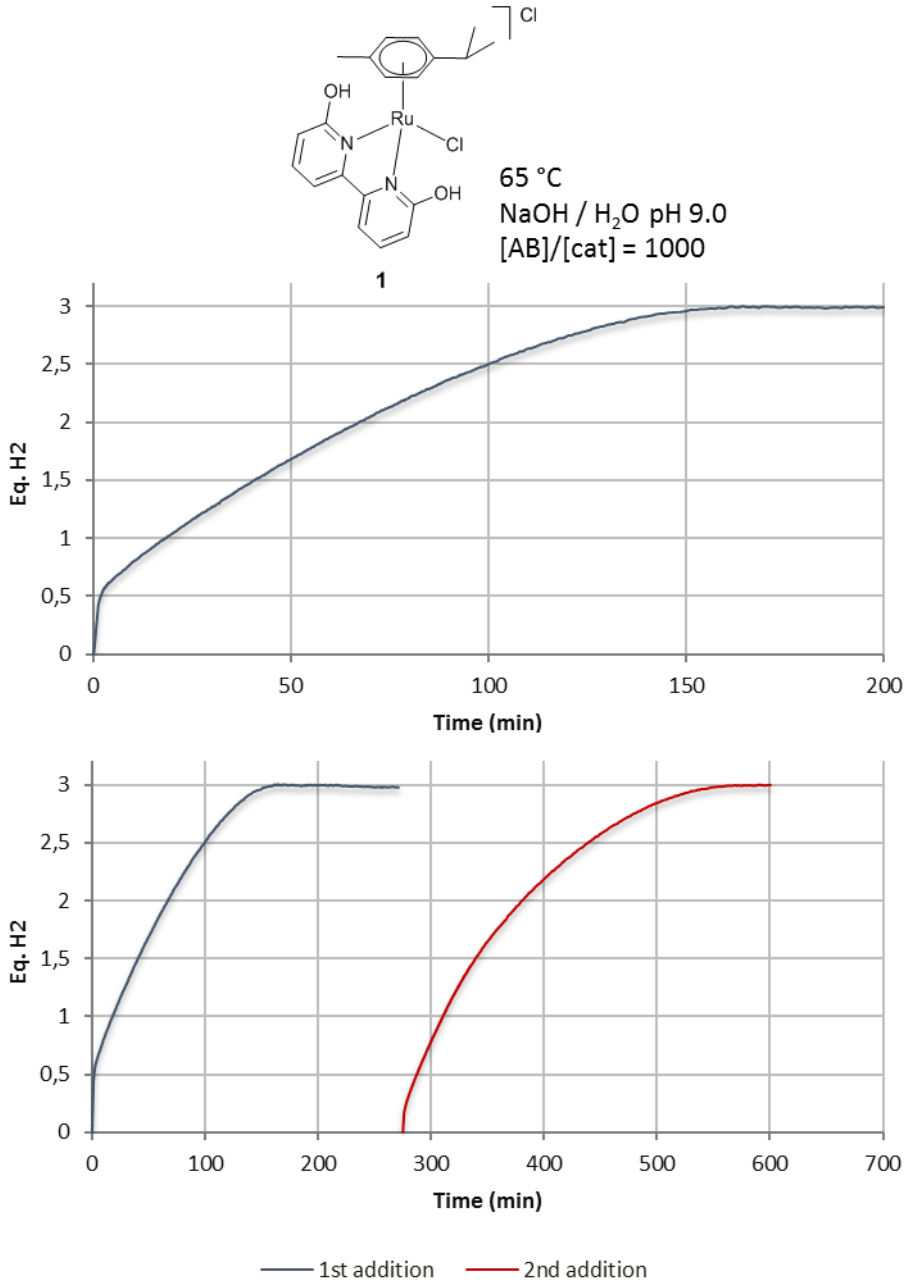


Figure S23. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 7). Conditions: [Ru] = 0.1 mM, [AB] = 0.1 M, 5 mL (H_2O, pH 9.0), 65 °C. Additional 15.4 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

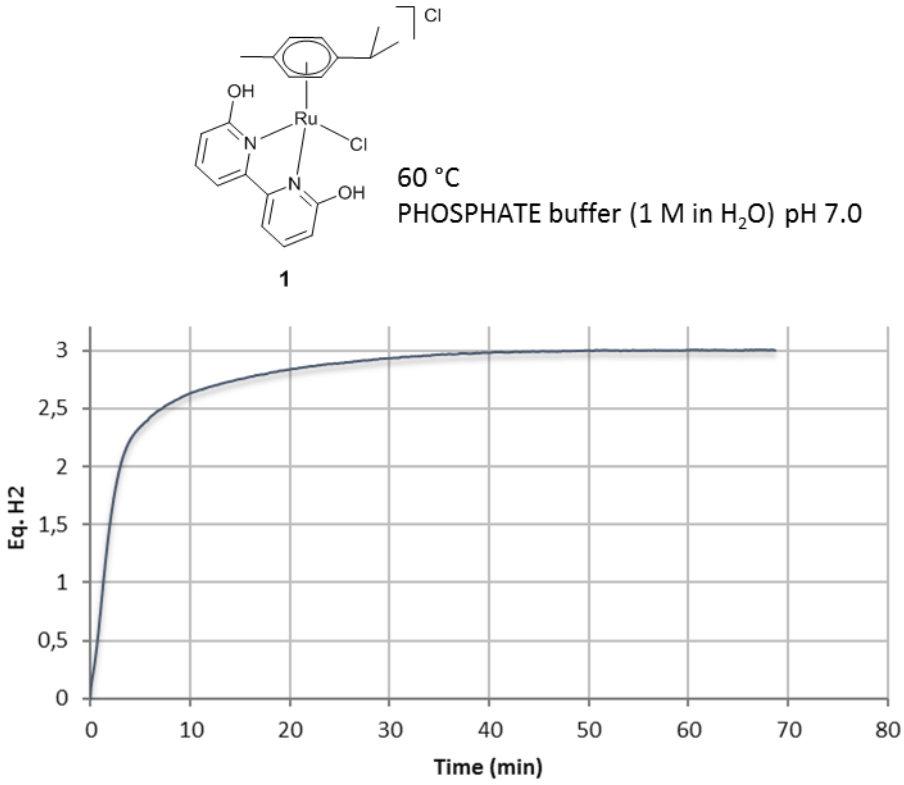


Figure S24. Reaction profile of AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL (phosphate buffer 1 M in H_2O, pH 7.0), 60 °C.

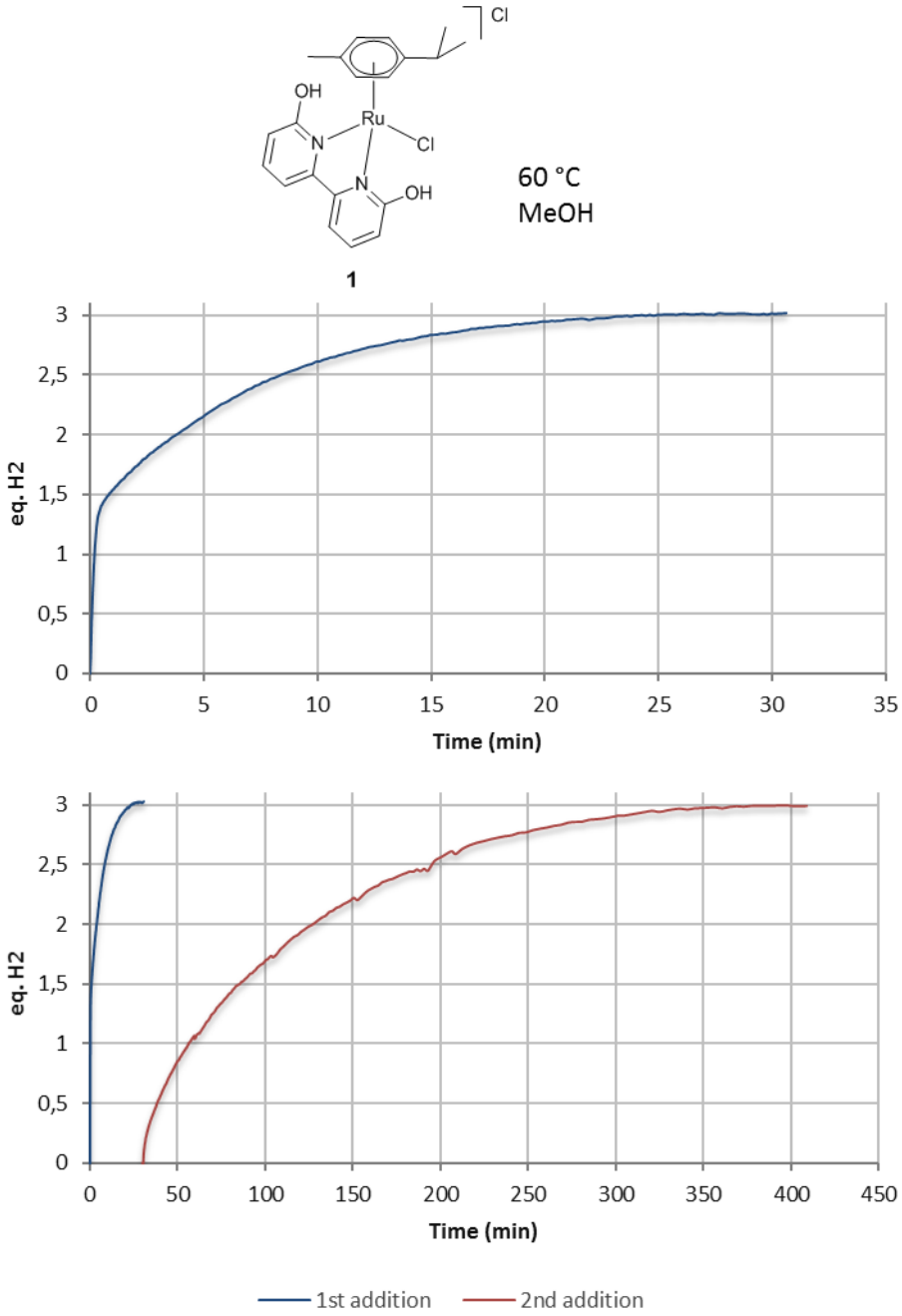


Figure S25. Reaction profiles of: TOP: AB alcoholysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 8). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL MeOH, 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

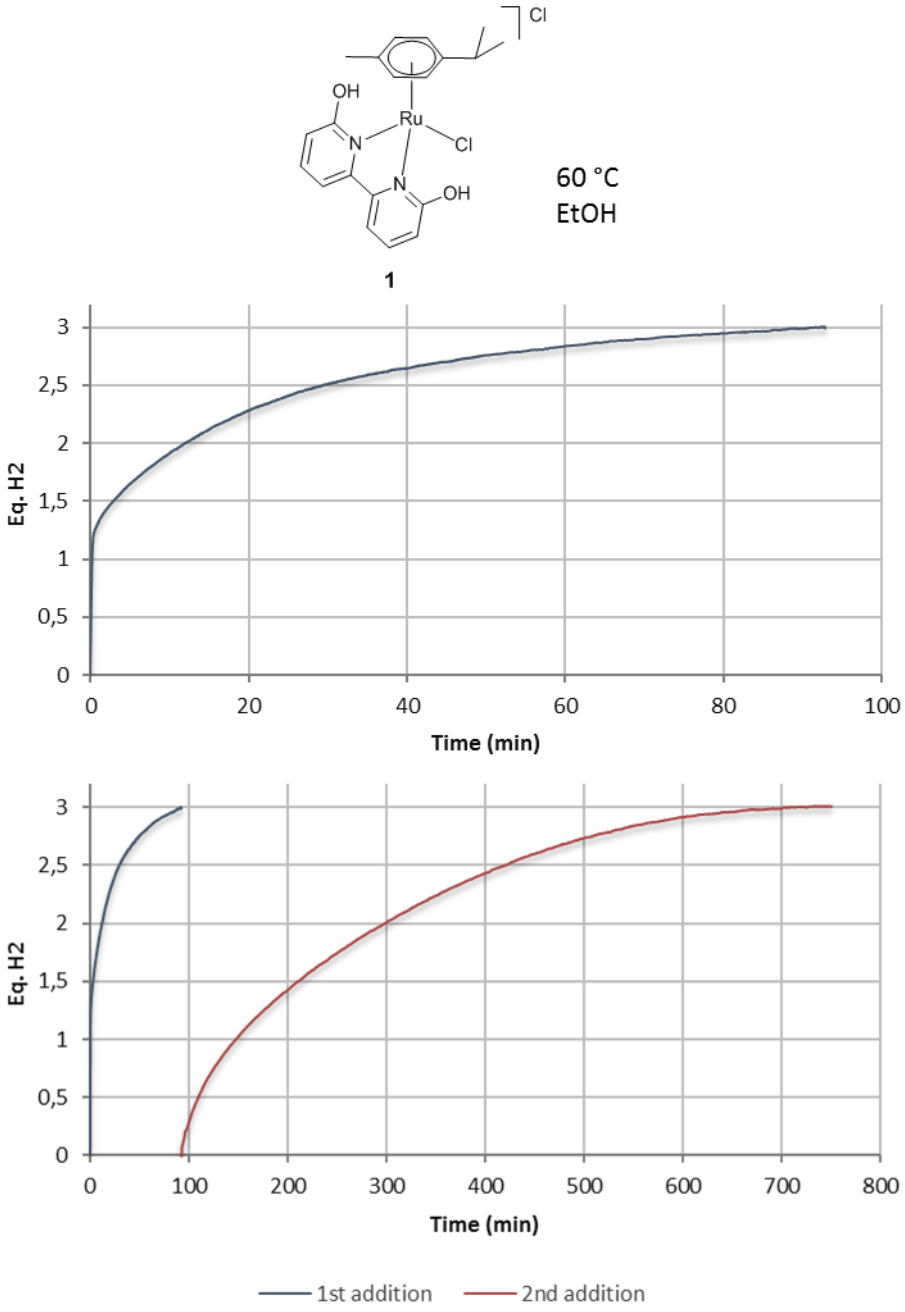


Figure S26. Reaction profiles of successive AB alcoholysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 9). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL EtOH, 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

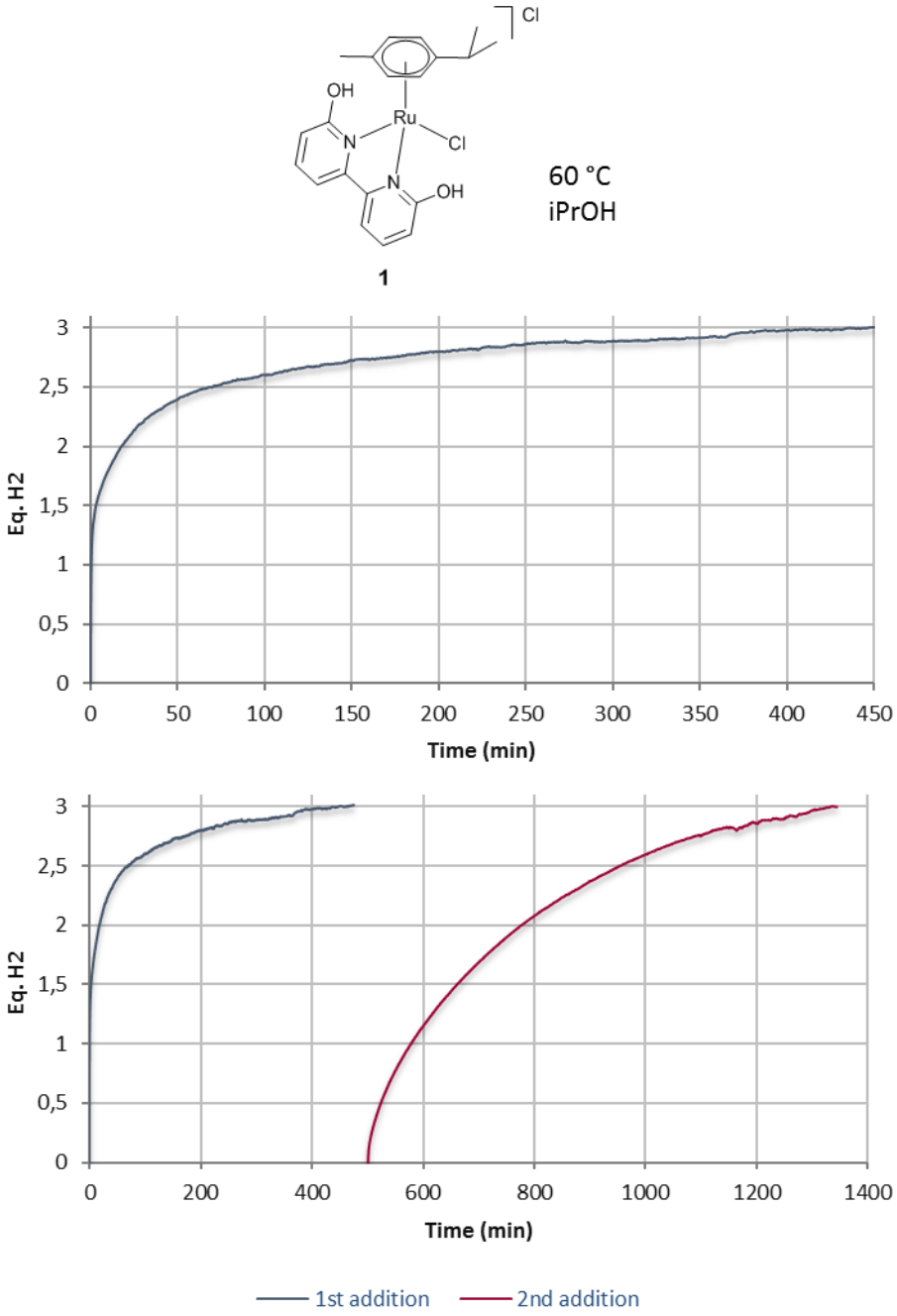


Figure S27. Reaction profiles of successive AB alcoholysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 10). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL iPrOH, 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

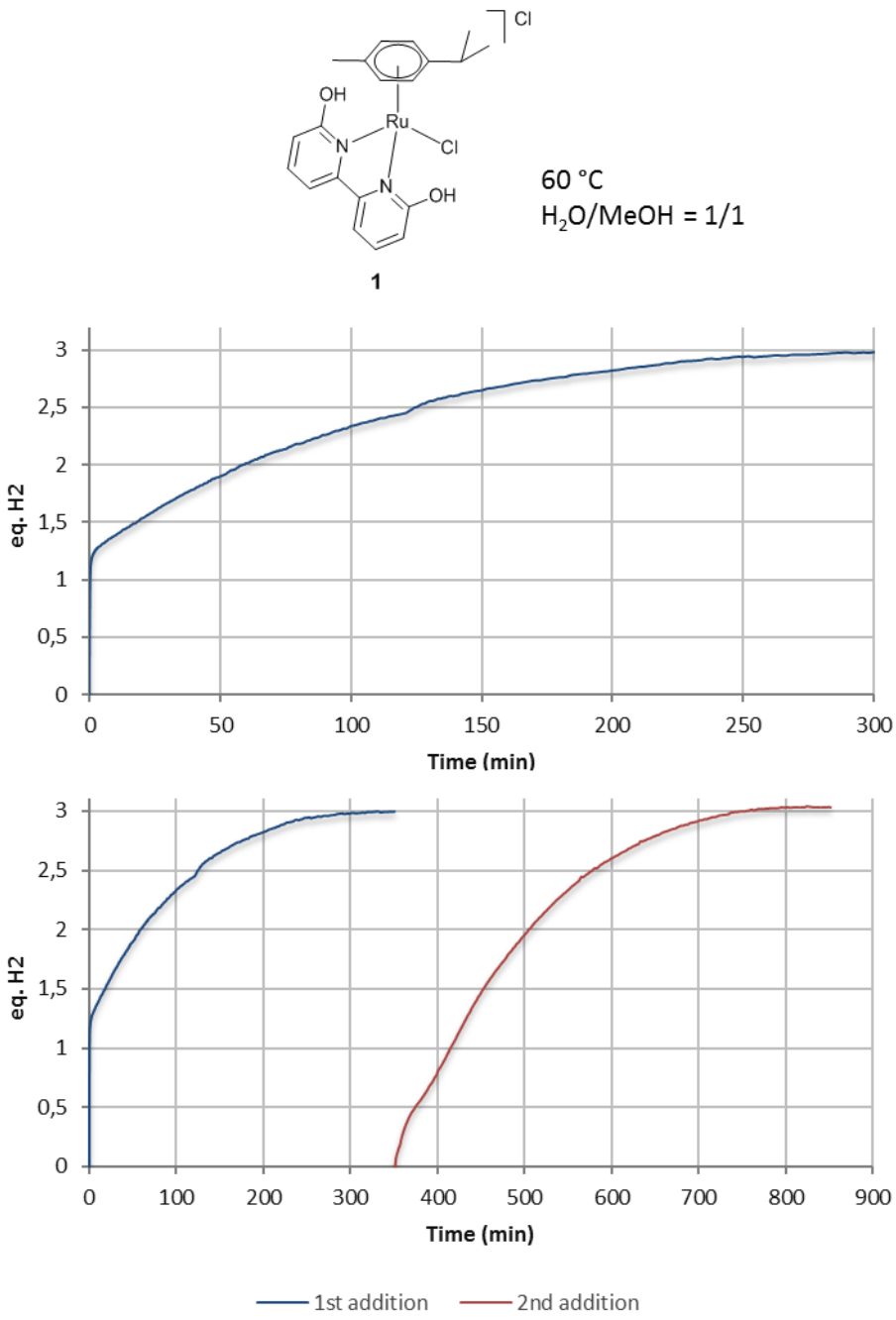


Figure S28. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 11). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O/MeOH = 1/1, 60 °C. Additional 21.3 mg of AB for the consecutive reaction. Sequential and superimposed reaction profiles shown.

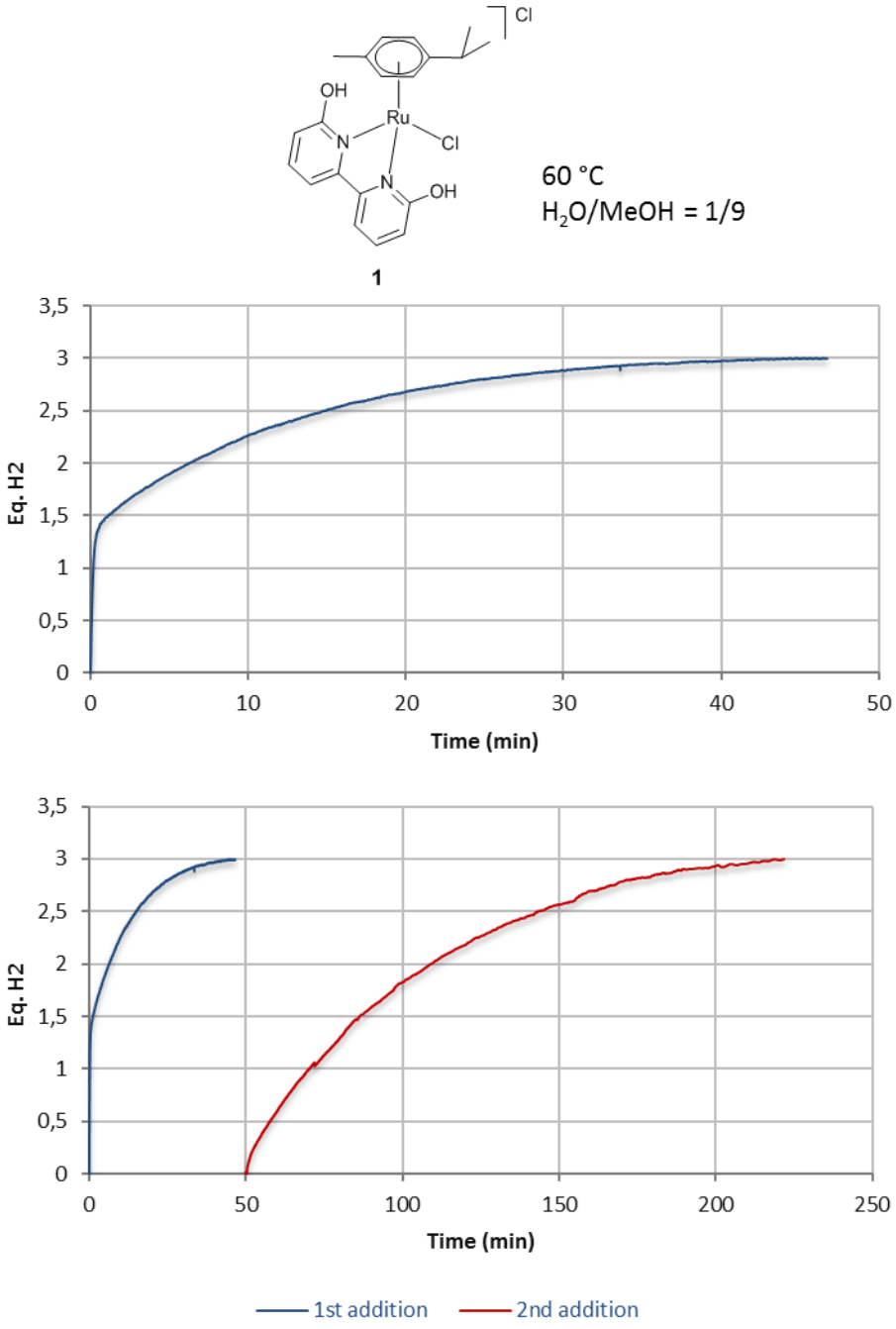


Figure S29. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 12). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O/MeOH = 1/9, 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

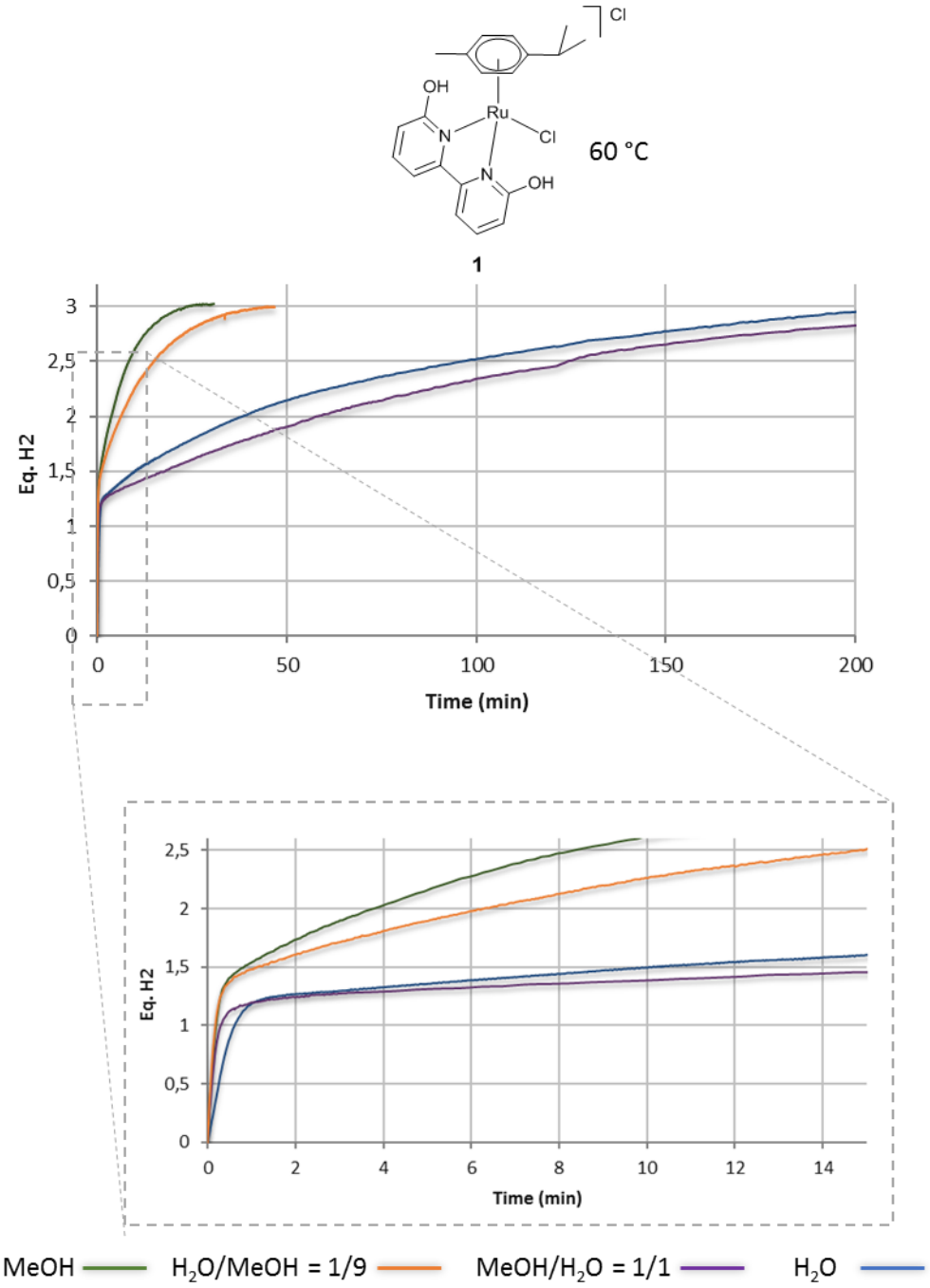


Figure S30. Comparative reaction profiles of AB solvolysis using different MeOH/H_2O mixtures as solvent and [Ru(p-Cym)(dhbp)Cl]Cl (**1**) as precatalyst. Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL solvent, 60 °C.

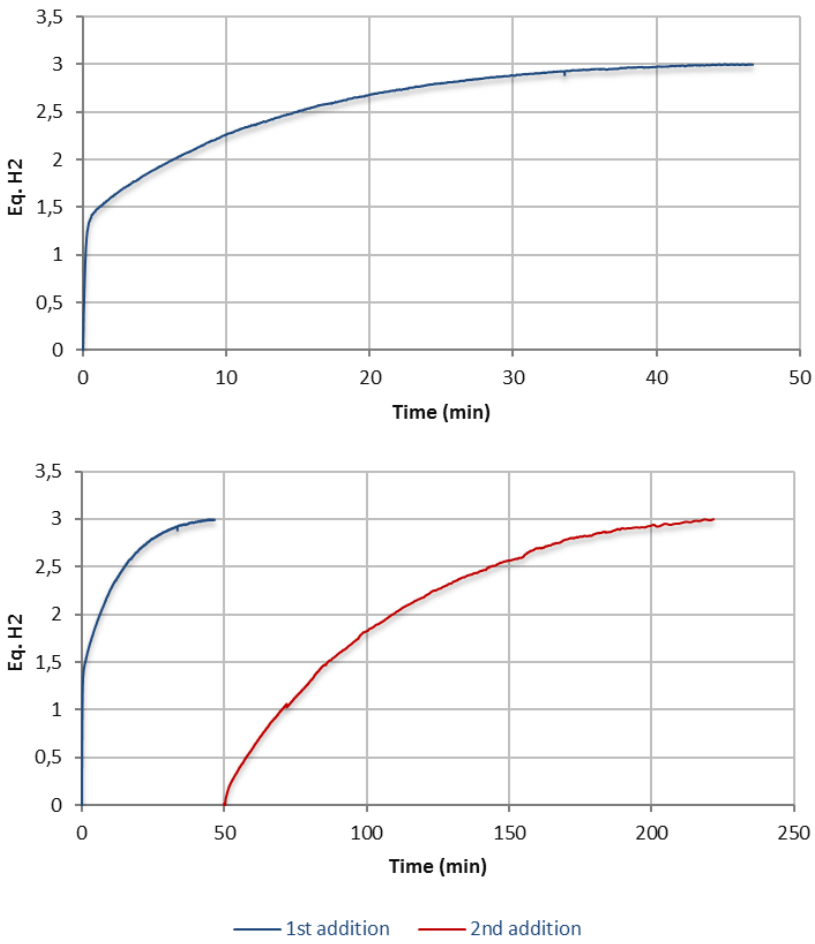


Figure S31. Reaction profiles of successive AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 13). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL NaOH 0.46 M in MeOH, 60 °C. BOTTOM: Reaction profiles of successive reactions.

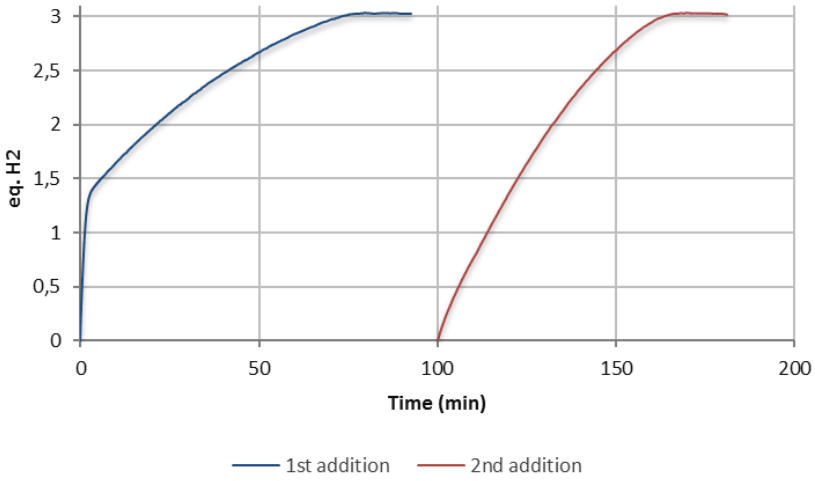


Figure S32 Reaction profiles of successive AB hydrolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 14). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 100 mg NaCl-modified molecular sieves, 1.5 mL H_2O, 60 °C. Additional 21.3 mg of AB for the consecutive reaction. BOTTOM: Reaction profiles of successive reactions.

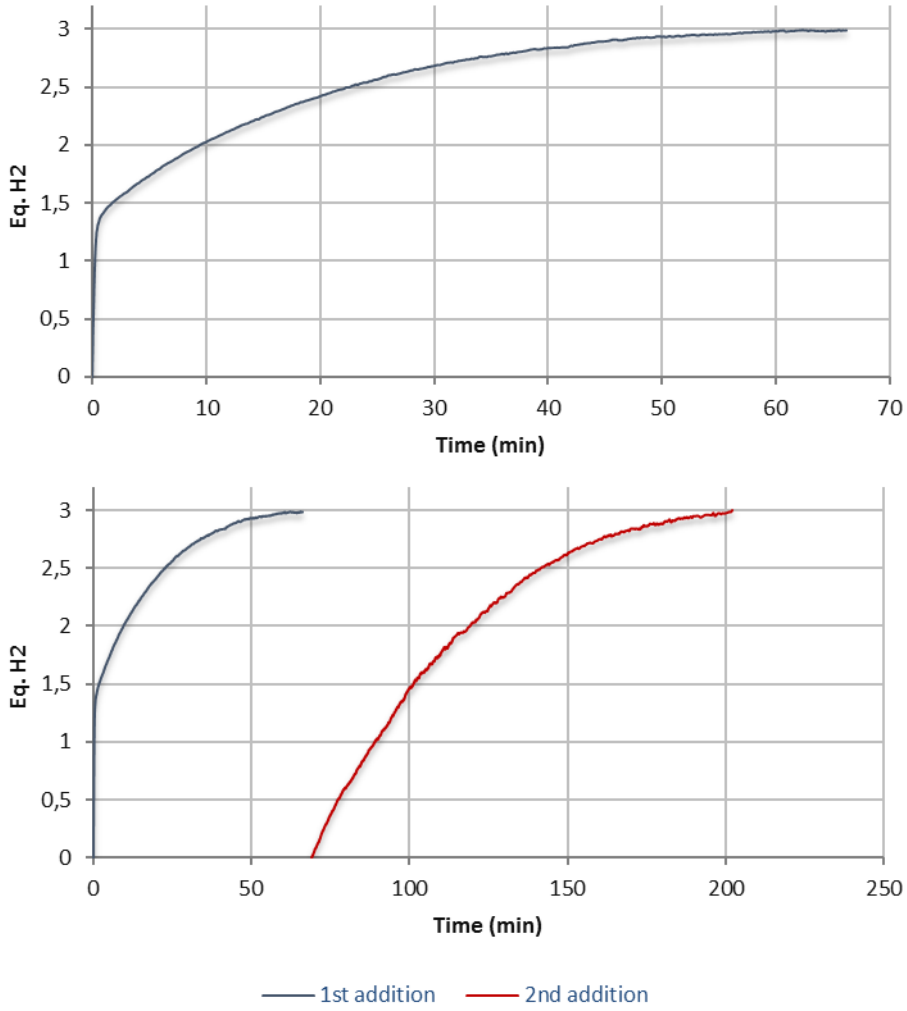


Figure S33. Reaction profiles of successive AB hydrolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 15). Conditions: [Ru] = 2.3 mM, [AB] = 0.46 M, 200 mg $MgSO_4$, 1.5 mL MeOH, 60 °C. BOTTOM: Reaction profiles of successive reactions.

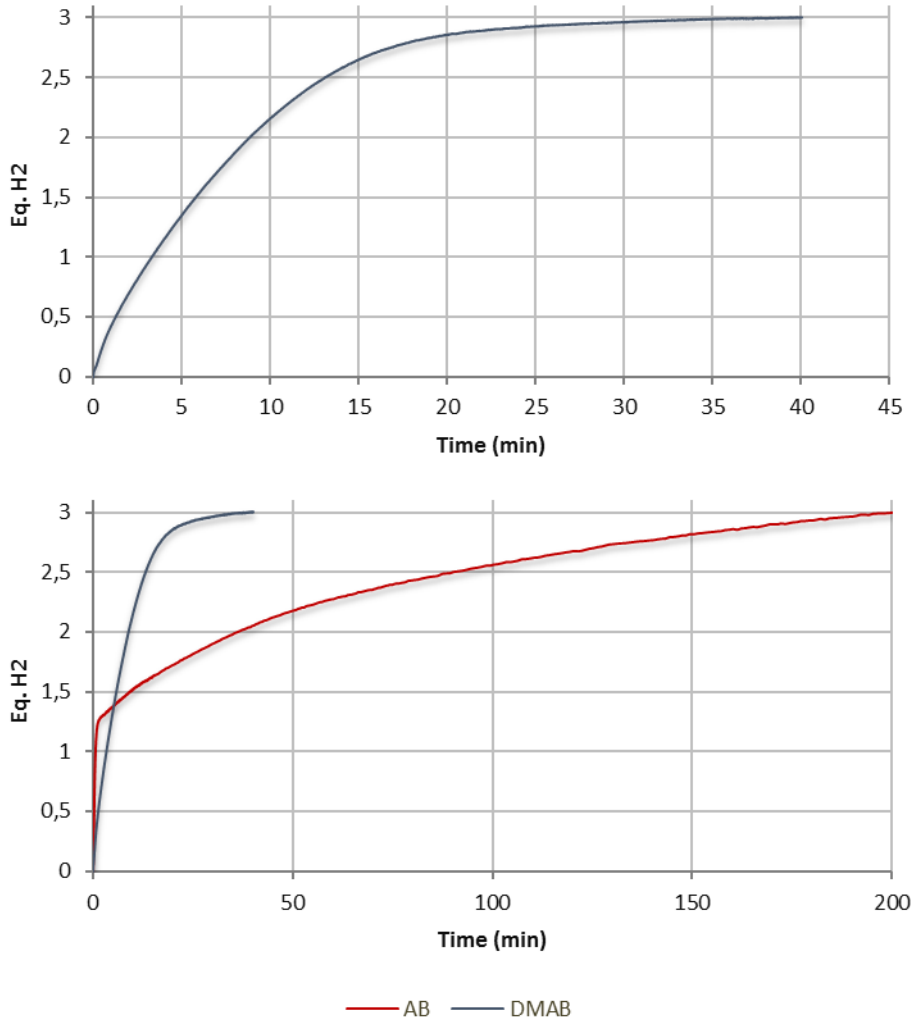


Figure S34. Reaction profiles of: TOP: $HMe_2N{\cdot}BH_3$ (DMAB) hydrolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table S1, Entry 1). Conditions: [Ru] = 2.3 mM, [DMAB] = 0.46 M, 1.5 mL H_2O, 60 °C. BOTTOM: Comparison of DMAB and AB hydrolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**) as precatalyst.

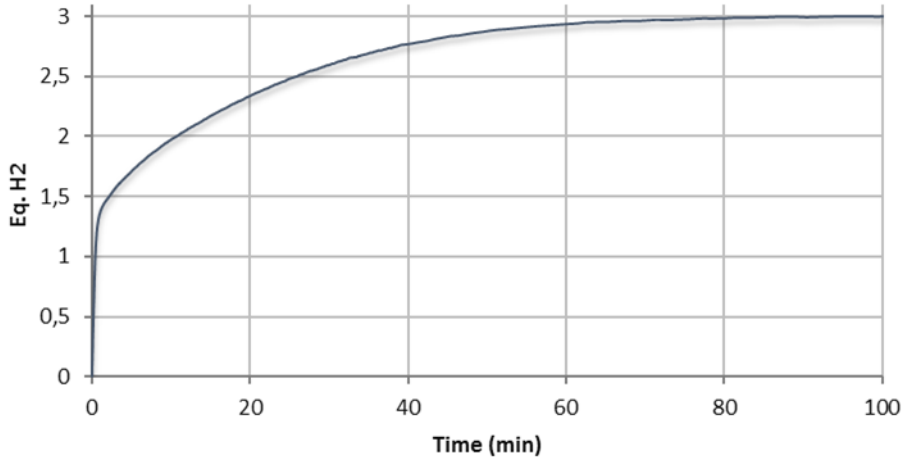


Figure S35. Reaction profile of DMAB alcoholysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table S1, Entry 2). Conditions: [Ru] = 2.3 mM, [DMAB] = 0.46 M, 1.5 mL MeOH, 60 °C.

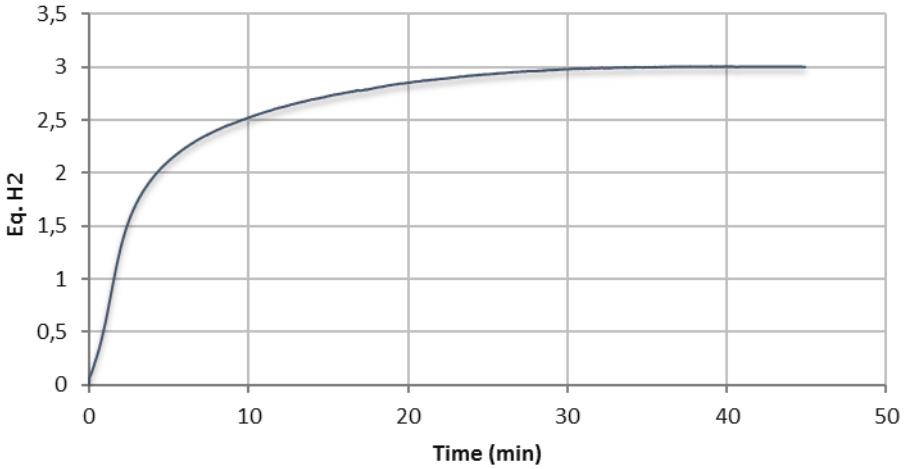


Figure S36. Reaction profile of DMAB hydrolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table S1, Entry 3). Conditions: [Ru] = 2.3 mM, [$HMe_2N{\cdot}BH_3$] = [NaOH] = 0.46 M, 1.5 mL H_2O, 60 °C.

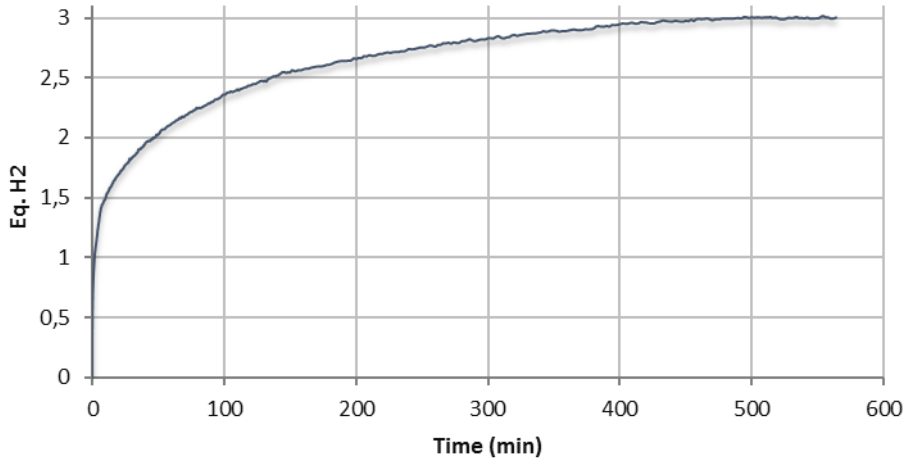
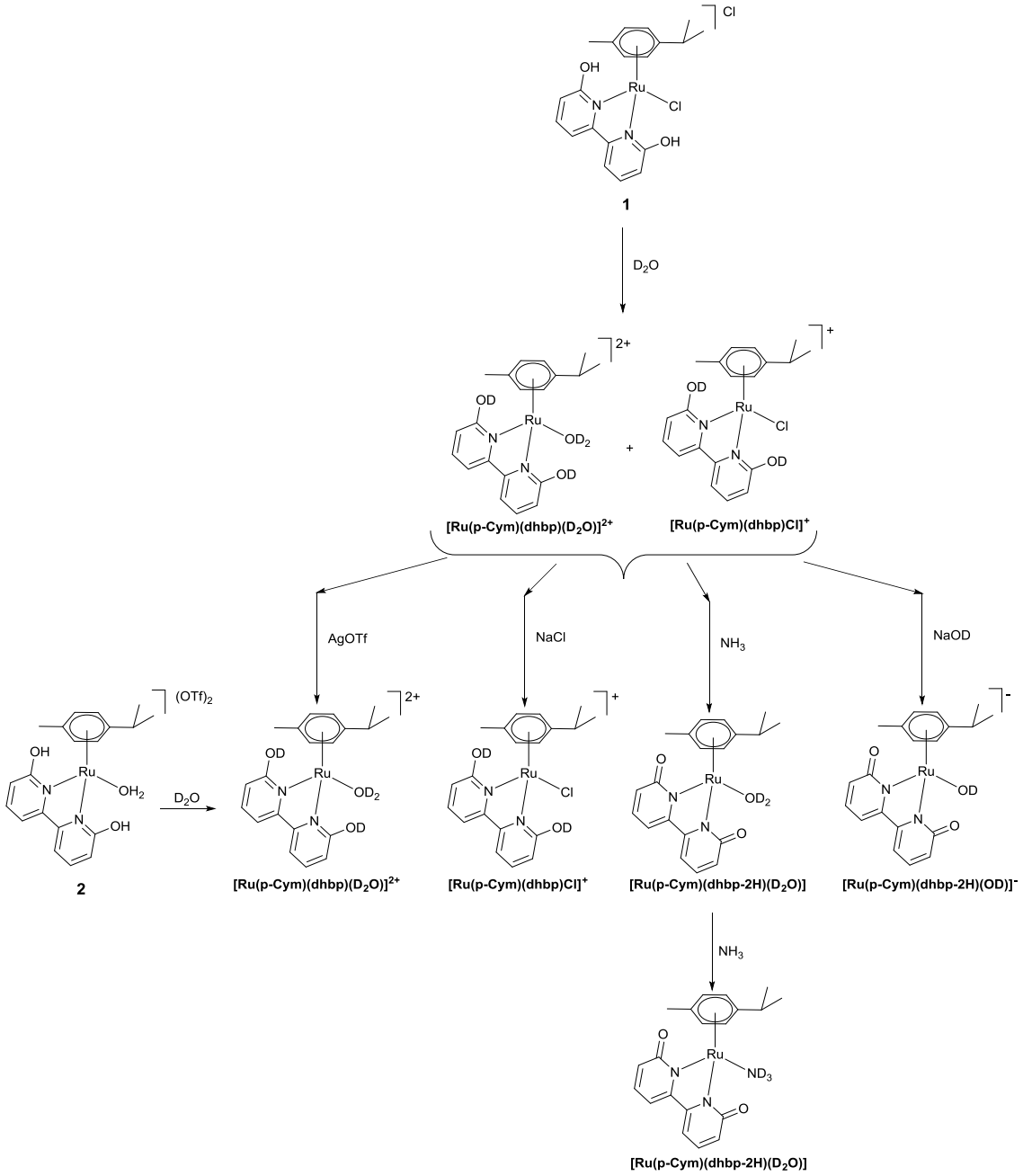


Figure S37. Reaction profile of DMAB alcoholysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table S1, Entry 4). Conditions: [Ru] = 2.3 mM, [DMAB] = [NaOH] = 0.46 M, 1.5 mL MeOH, 60 °C.

Table S1. Catalytic results. DMAB solvolysis using precatalysts **1**.

Entry	Solvent	$TOF_{10\%}$ (h^{-1})	$TOF_{50\%}$ (h^{-1})	Total time[a]
1	H_2O	1627	1032	35 min
2	MeOH	12414	2775	80 min
3[b]	NaOH/H_2O	2239	2521	35 min
4[b]	NaOH/MeOH	11921	589	3 h

Reaction conditions: [cat] = $2.3{\cdot}10^{-3}$ M, [DMAB] = 0.46 M, 1.5 mL solvent, 60 °C. [a] Time to reach full conversion. [b] [NaOH] = 0.46 M.



Scheme S1. Reactivity scheme used for the *in situ* characterizations in D_2O.

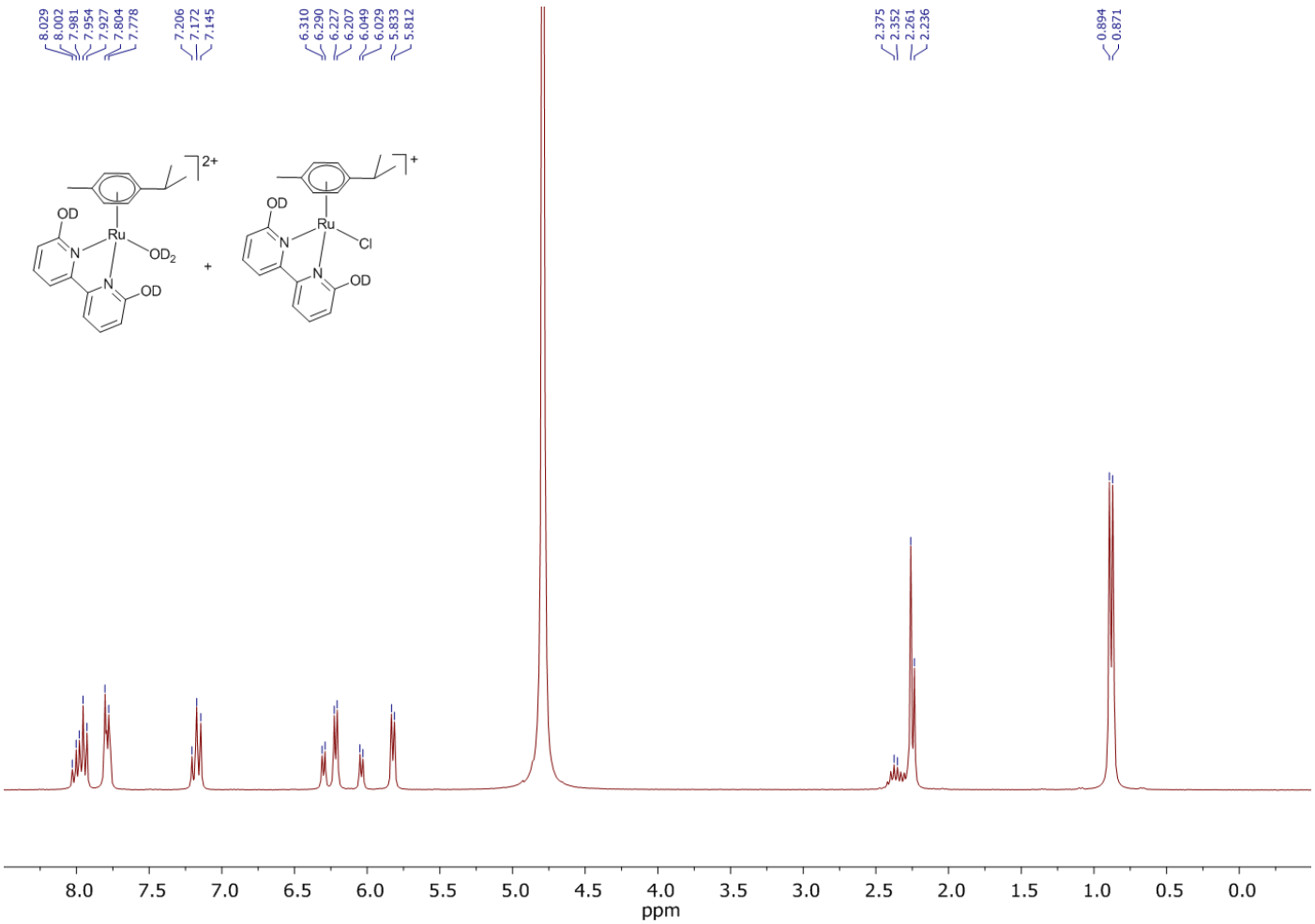


Figure S38. ^{1}H NMR spectra (300 MHz). 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O.

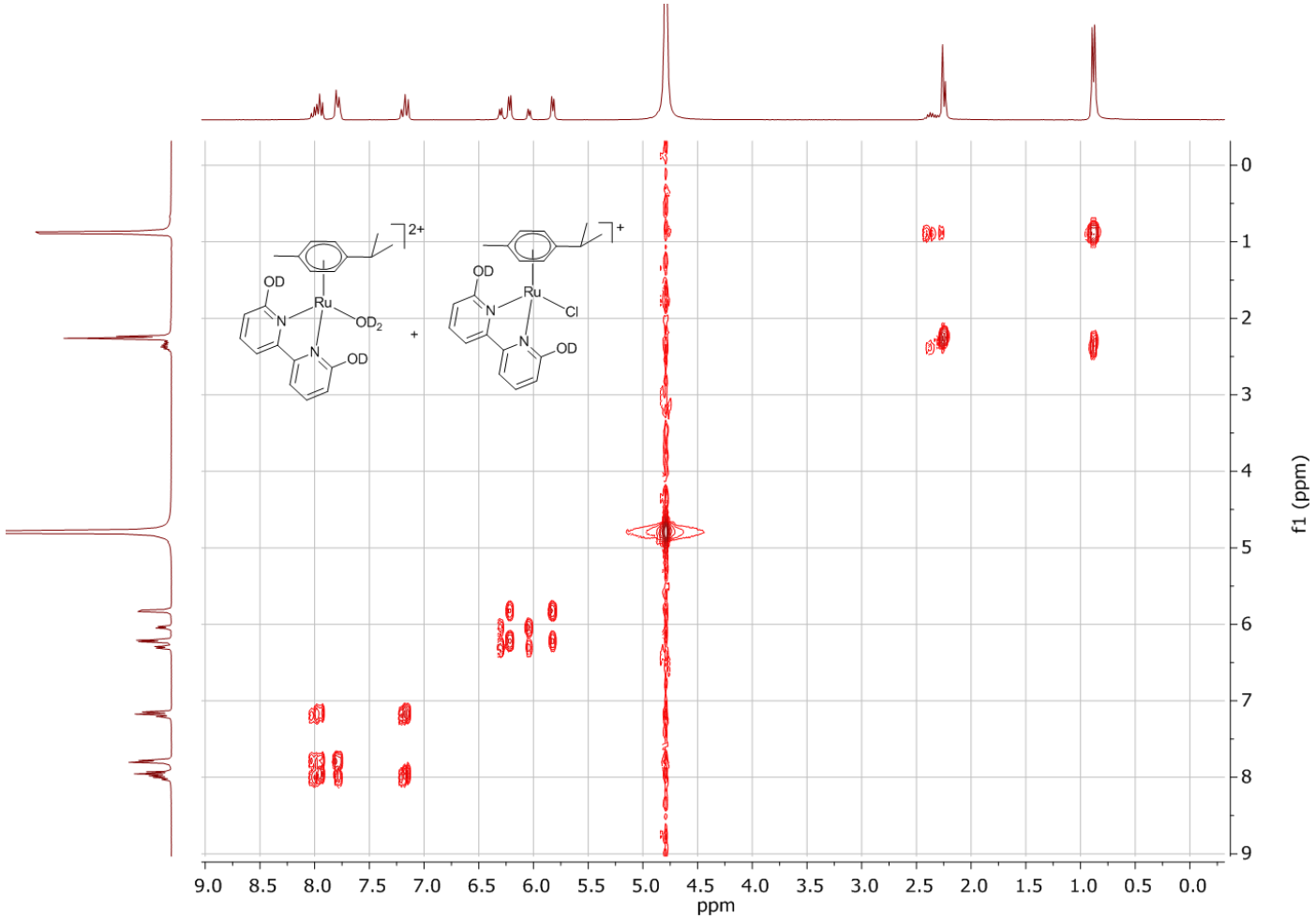


Figure S39. COSY NMR spectra (300 MHz). 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O.

***In situ* formation and characterization of [Ru(p-Cym)(dhbp)Cl]$^{+}$ (D_2O):**

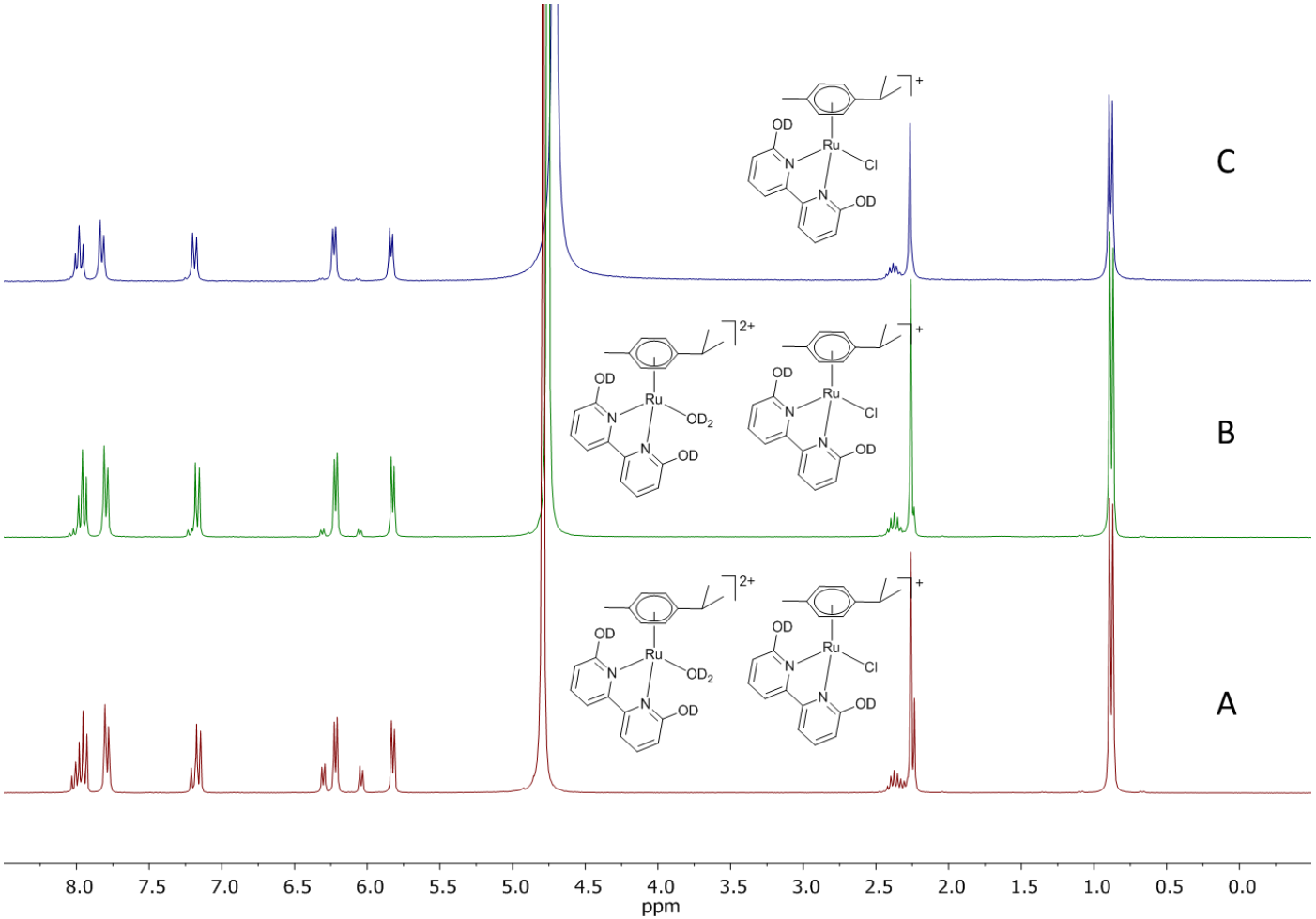


Figure S40. ^{1}H NMR spectra (300 MHz). 3.16 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) and in 0.5 mL of D_2O. **B:** After addition of 10 mg of NaCl. **B:** After addition of 15 mg more of NaCl.

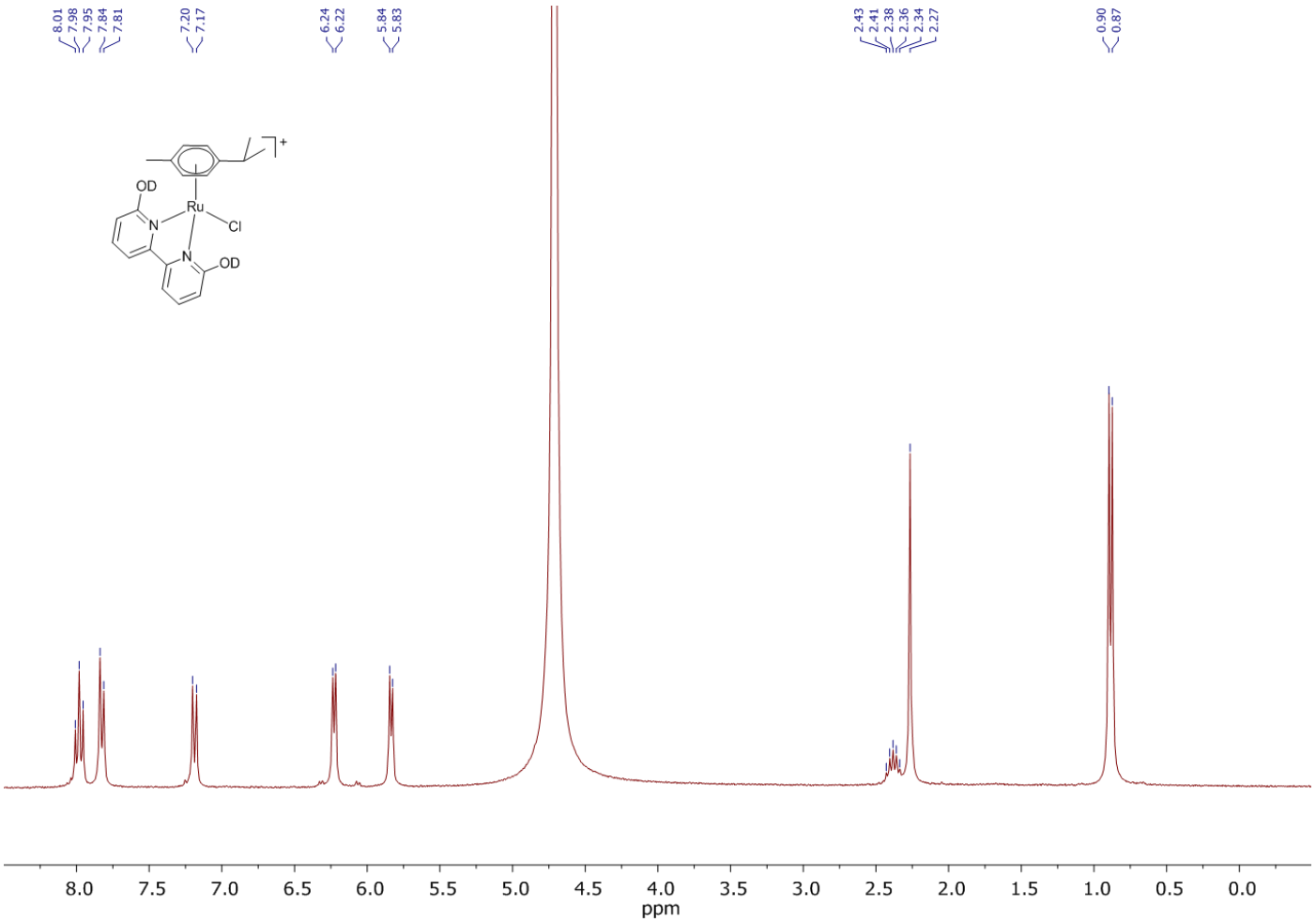


Figure S41. ^{1}H NMR spectra (300 MHz). 3.16 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 25 mg of NaCl.

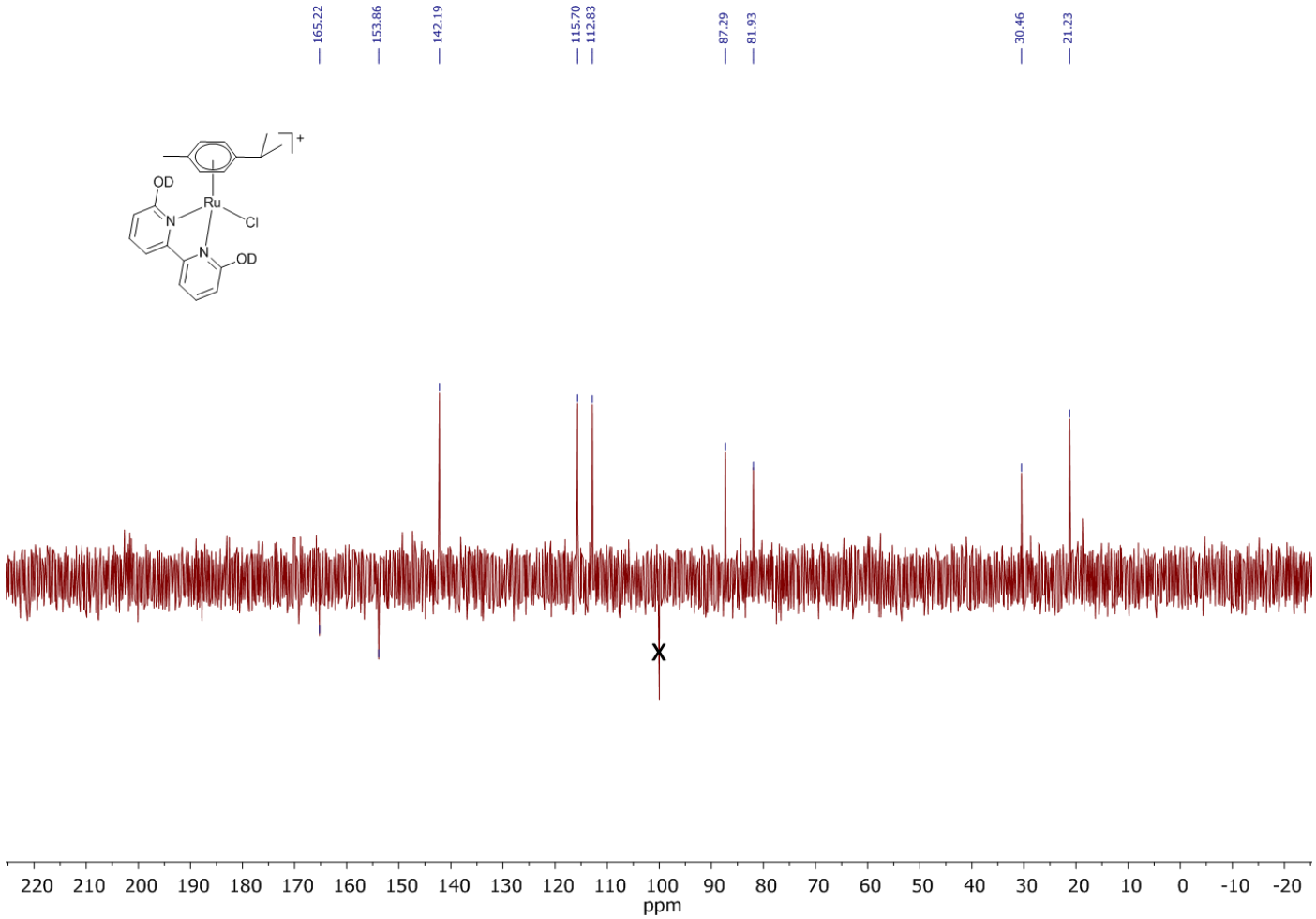


Figure S42. ^{13}C(APT) NMR spectra (75 MHz). 3.16 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 25 mg of NaCl. One of the quaternary carbons of p-Cymene is hidden in the background noise of the spectra. Peak at 100 ppm is an artifact (center of the acquisition window).

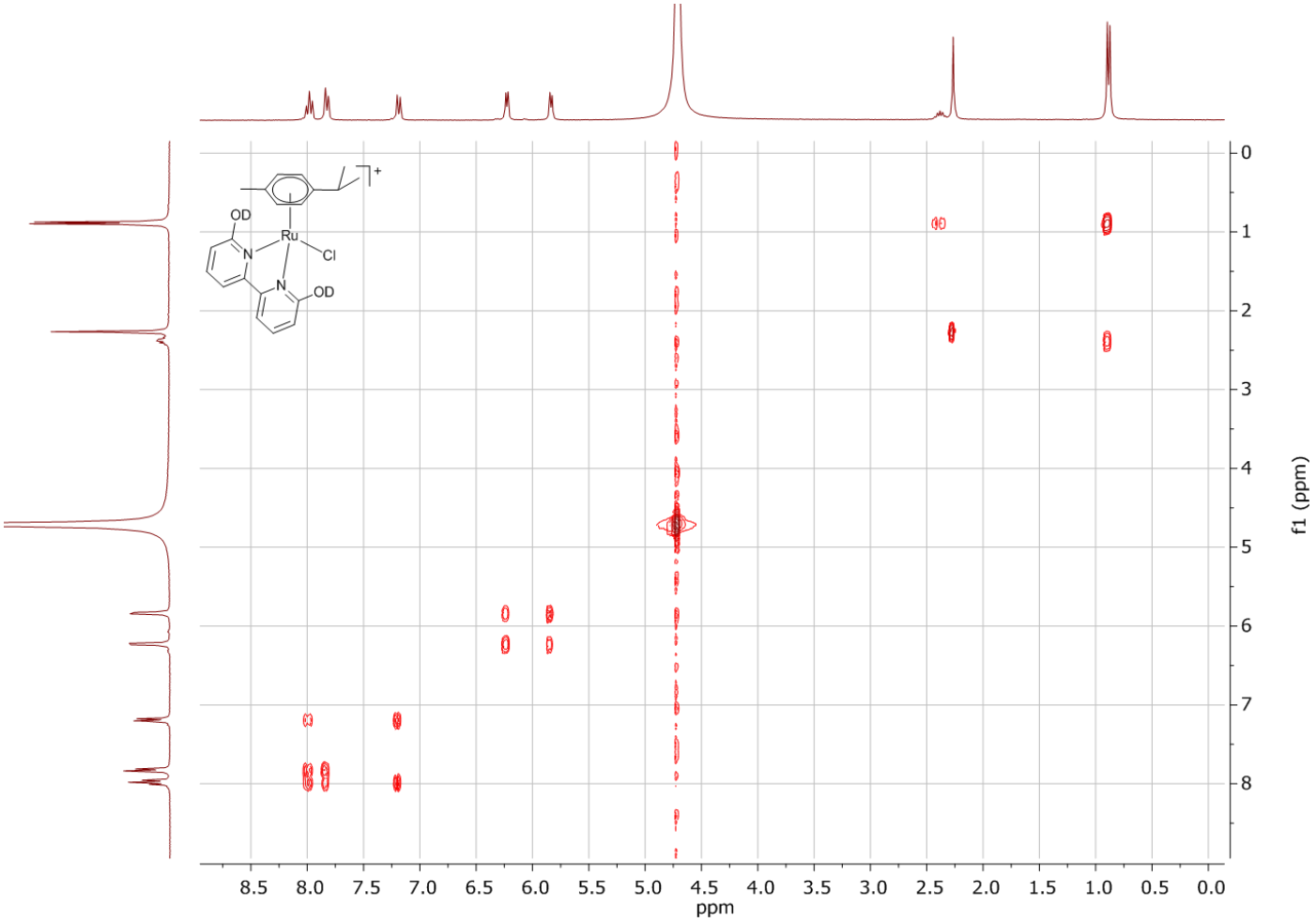


Figure S43. COSY NMR spectra (300 MHz). 3.16 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 25 mg of NaCl.

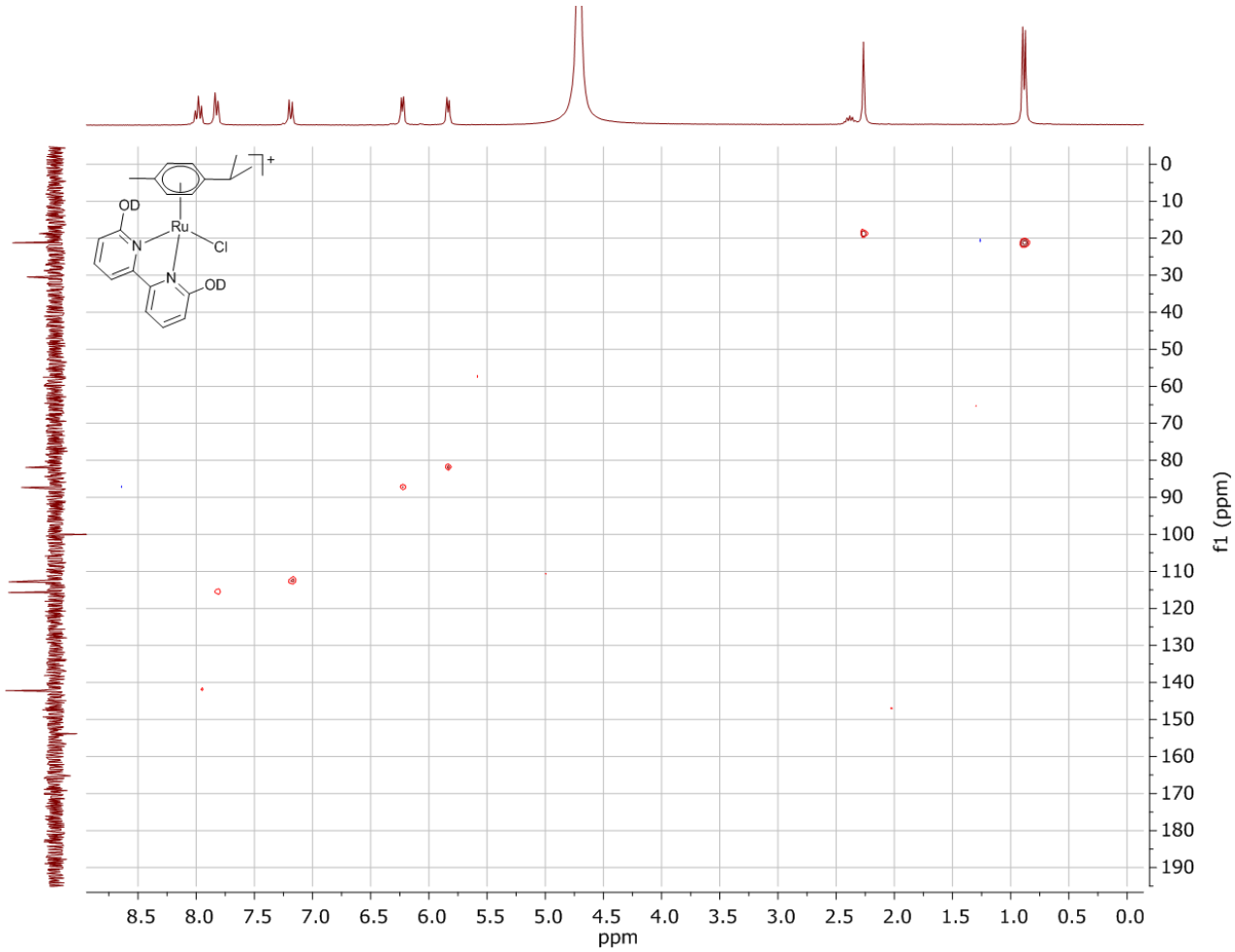


Figure S44. HSQC NMR spectra (300 MHz). 3.16 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 25 mg of NaCl.

***In situ* formation and characterization of [Ru(p-Cym)(dhbp)(D_2O)]$^{2+}$ (D_2O):**

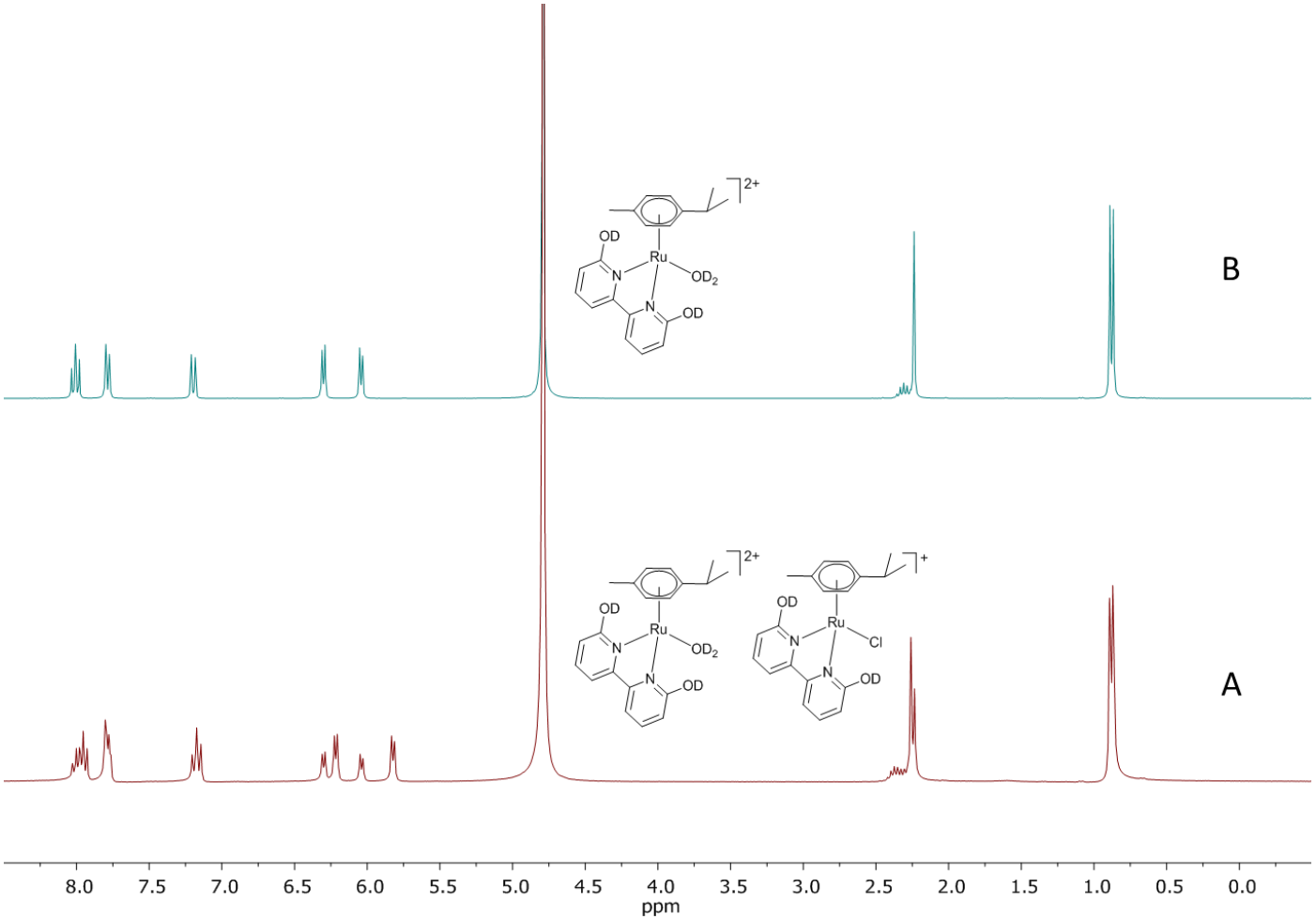


Figure S45. ^{1}H NMR spectra (300 MHz). 3.65 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) and in 0.5 mL of D_2O. **B:** After addition of 10 mg of AgOTf.

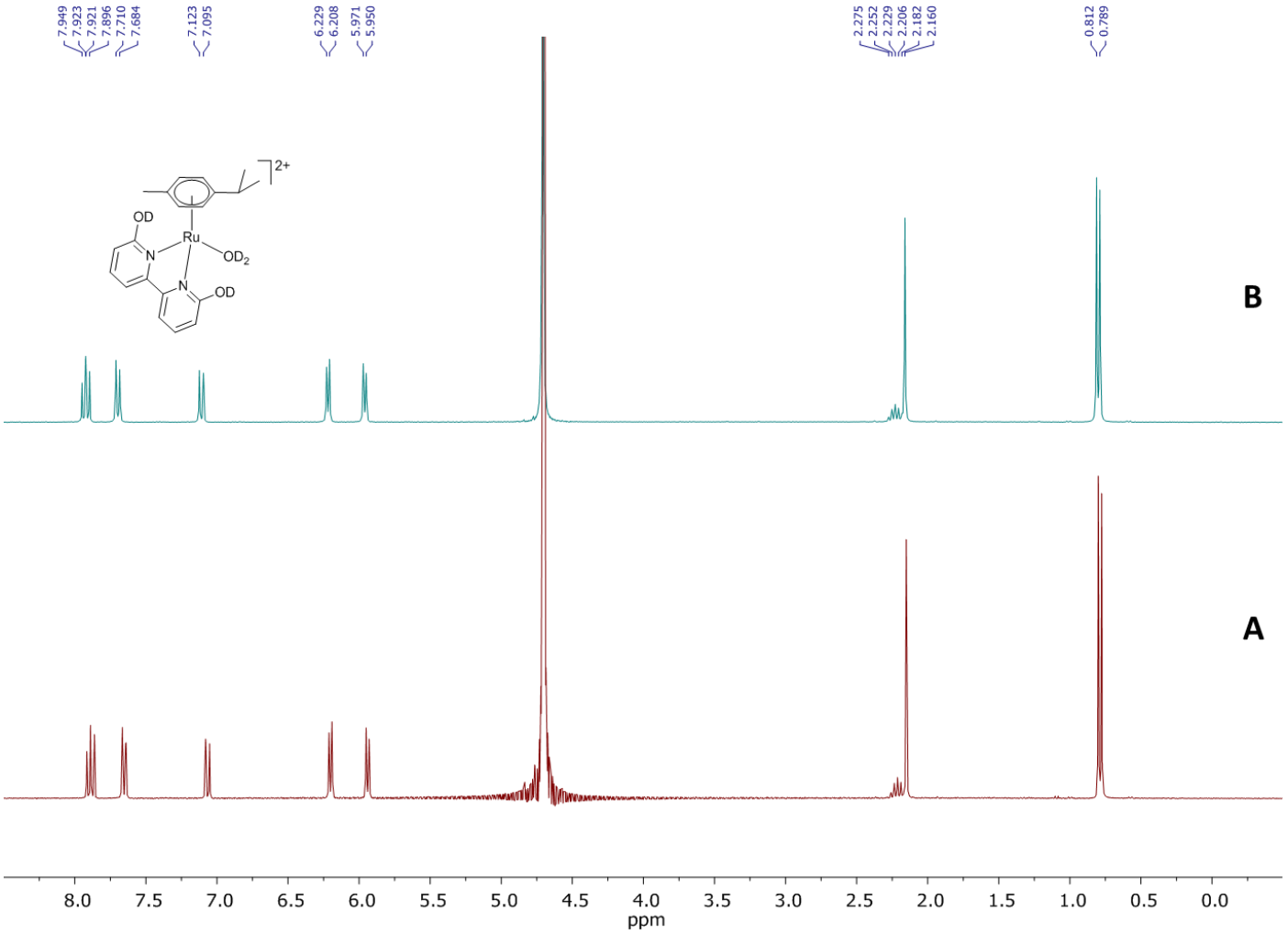


Figure S46.[1]H NMR spectra (300 MHz). **A.** 1.24 mg of [Ru(p-Cym)(dhbp)(H_2O)](OTf)$_2$ (**2**) in 0.5 mL of D_2O. **B.** 3.65 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 10 mg of AgOTf.

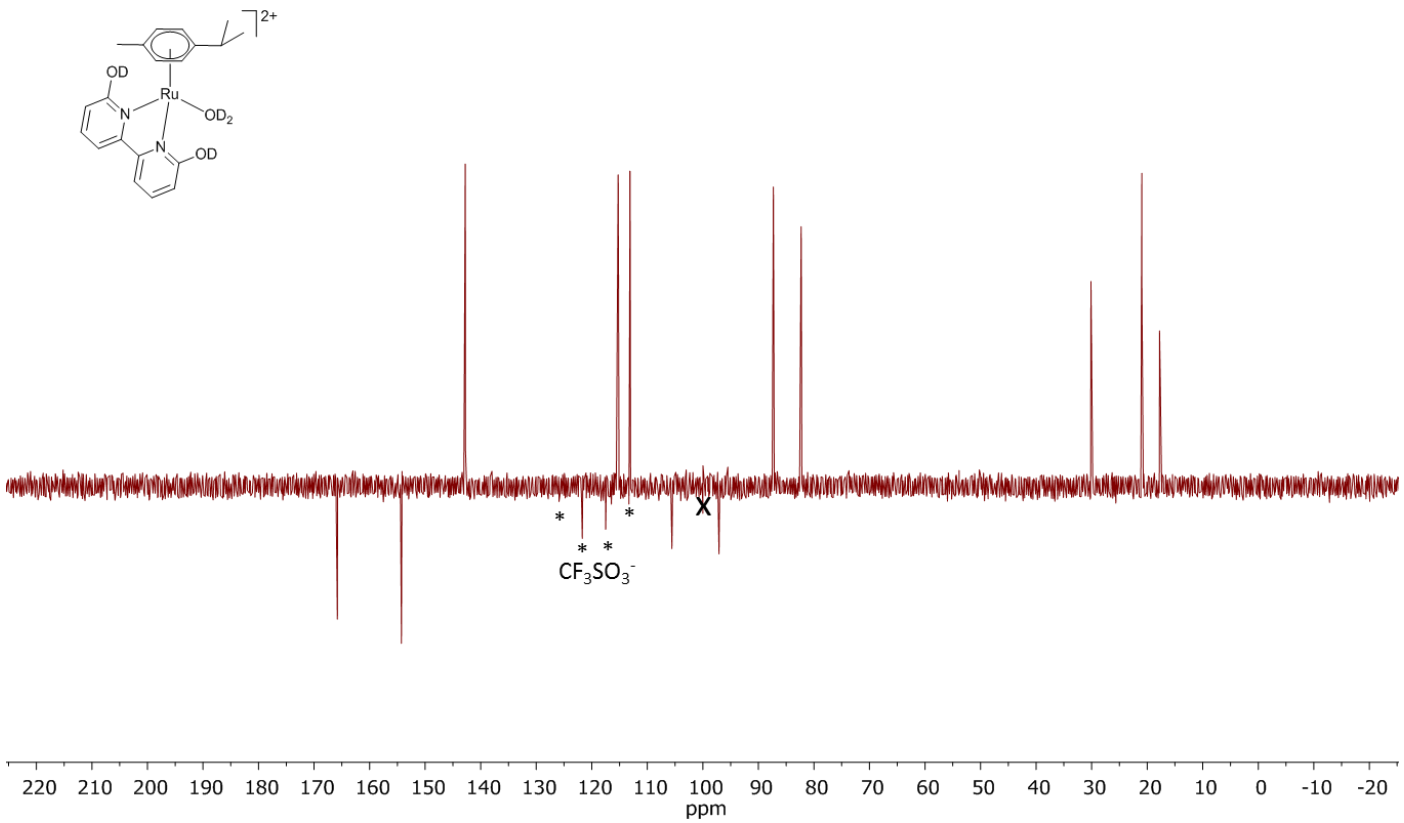


Figure S47. ^{13}C(APT) NMR spectra (75 MHz). 3.65 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 10 mg of AgOTf. Peak at 100 ppm is an artifact (center of the acquisition window).

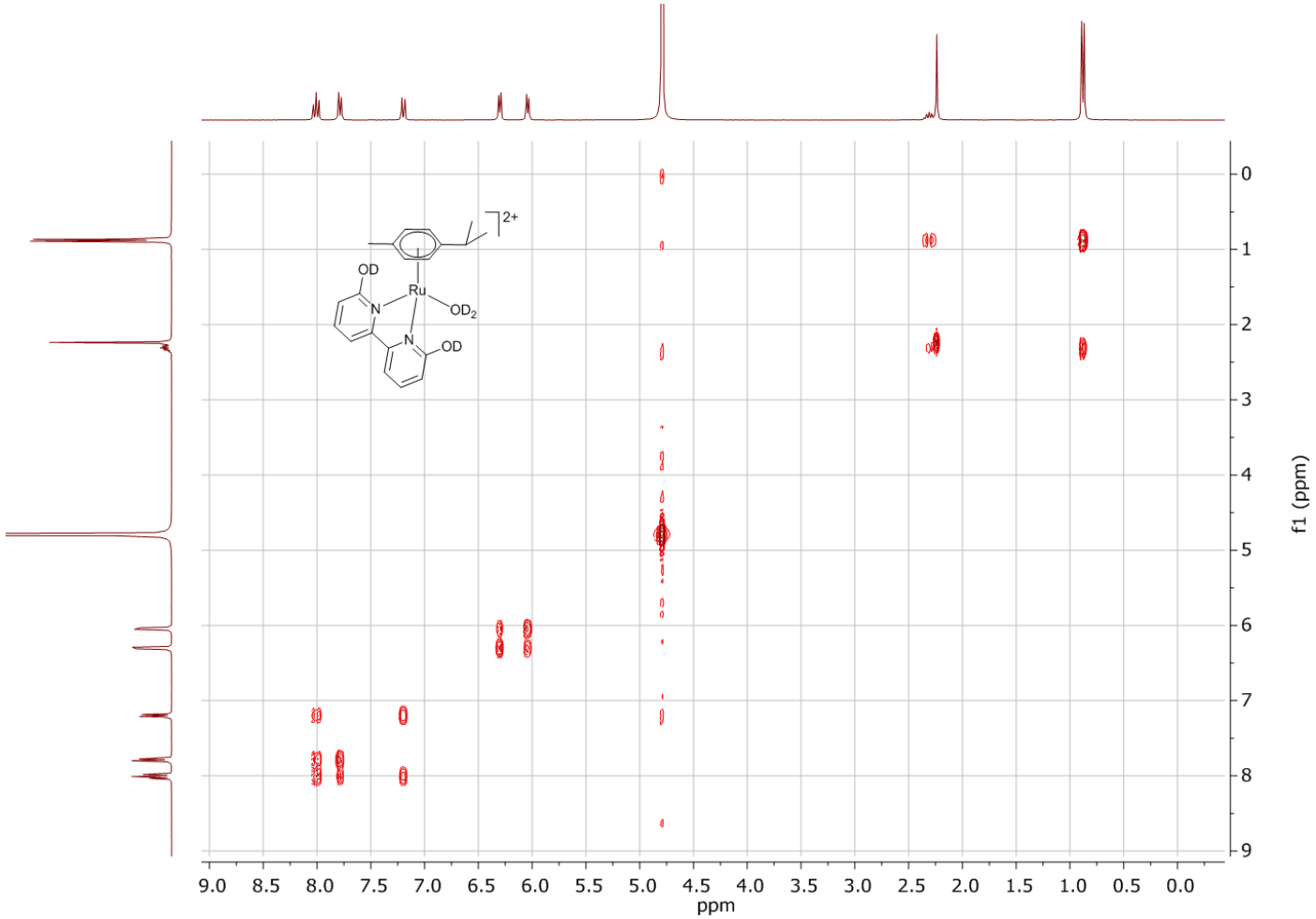


Figure S48. COSY NMR spectra (300 MHz). 3.65 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 10 mg of AgOTf.

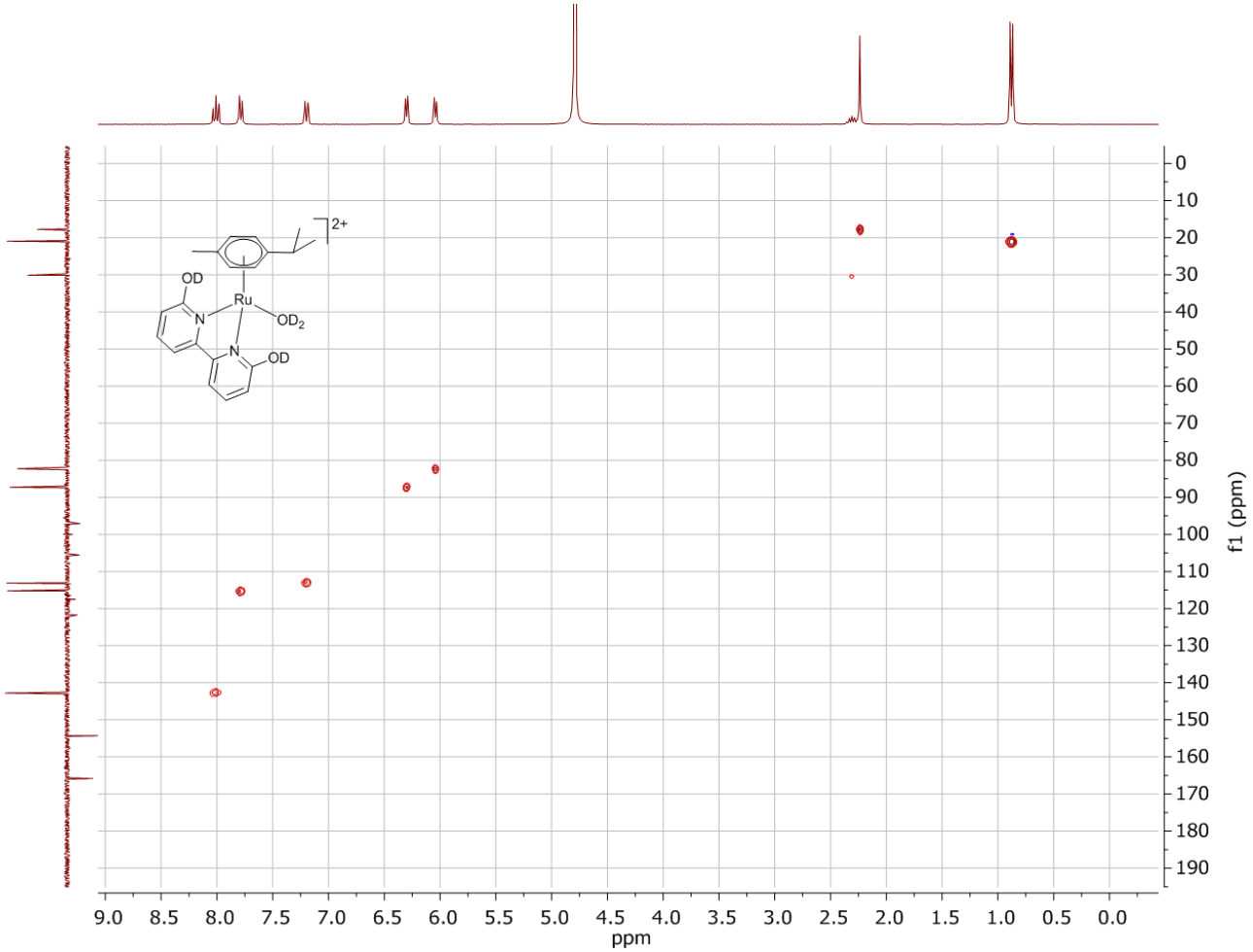


Figure S49 HSQC NMR spectra (300 MHz). 3.65 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 10 mg of AgOTf.

***In situ* formation and characterization of [Ru(p-Cym)(dhbp-2H)(ND_3)] (D_2O):**

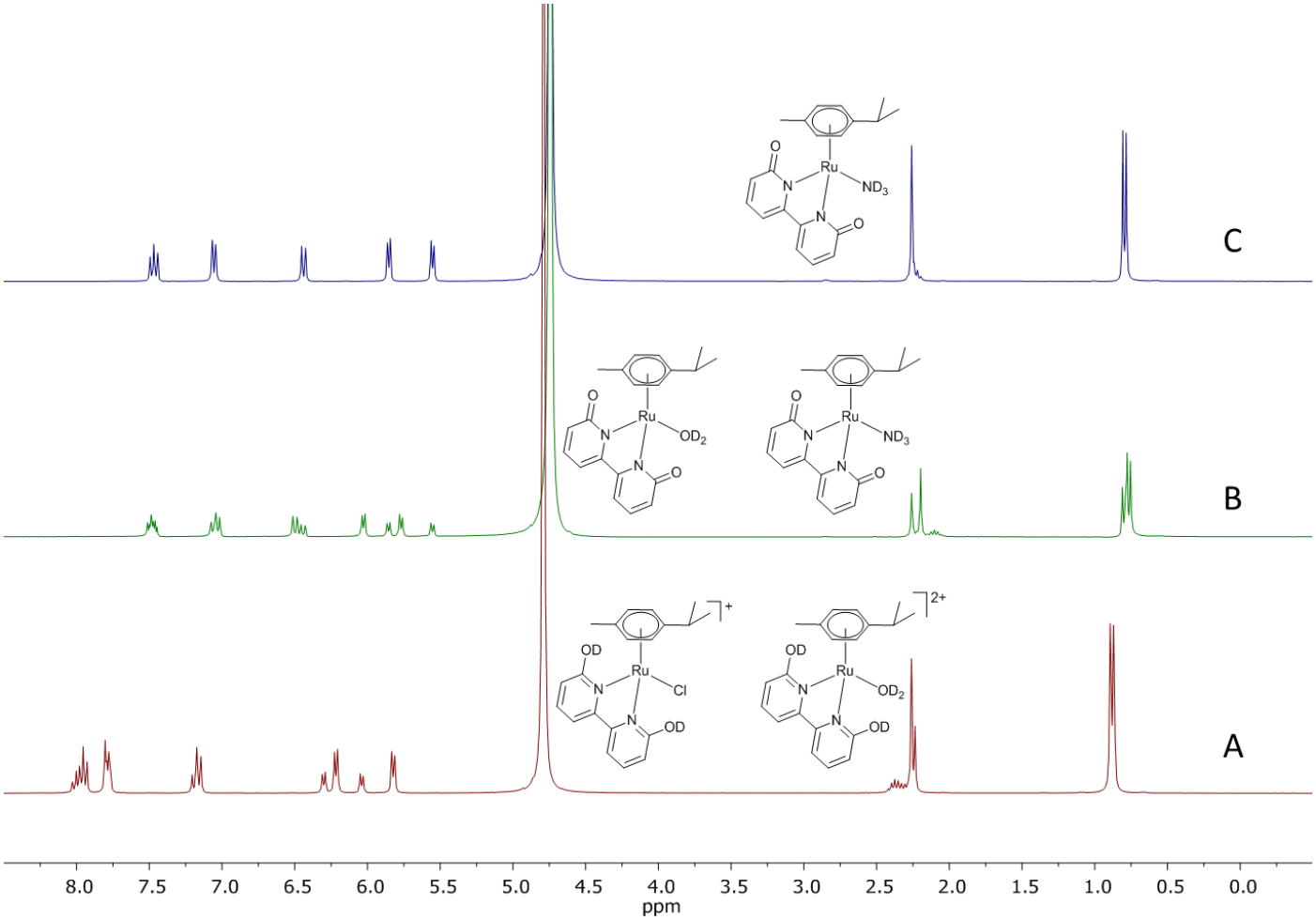


Figure S50.^{1}H NMR spectra (300 MHz). 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O. **B:** After addition of 10 µL of NH_3 (20% v/v in H_2O). **C:** After addition of 10 µL more of NH_3 (20% v/v in H_2O).

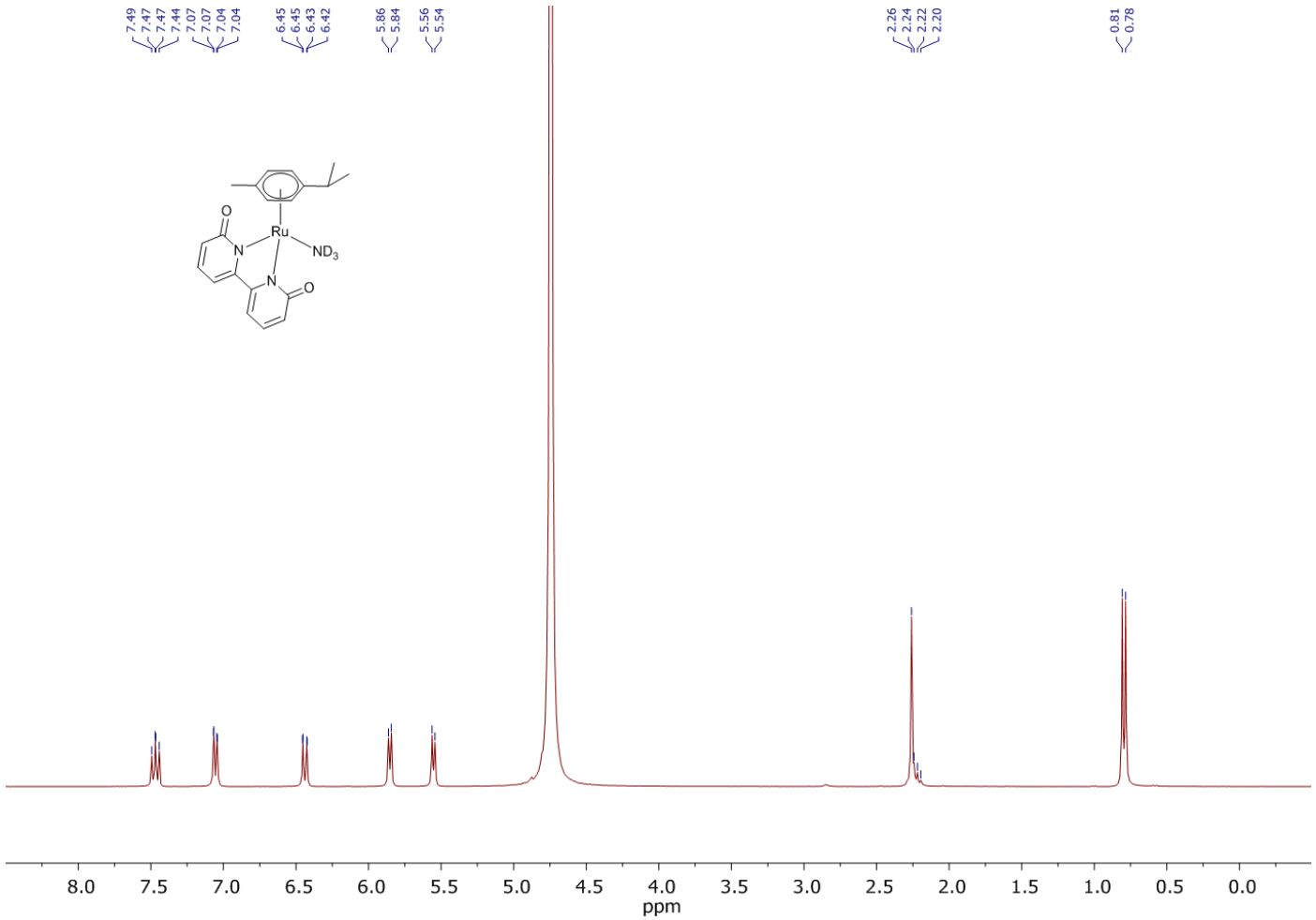


Figure S51. ^{1}H NMR spectra (300 MHz). 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 20 µL of NH_3 (20% v/v in H_2O).

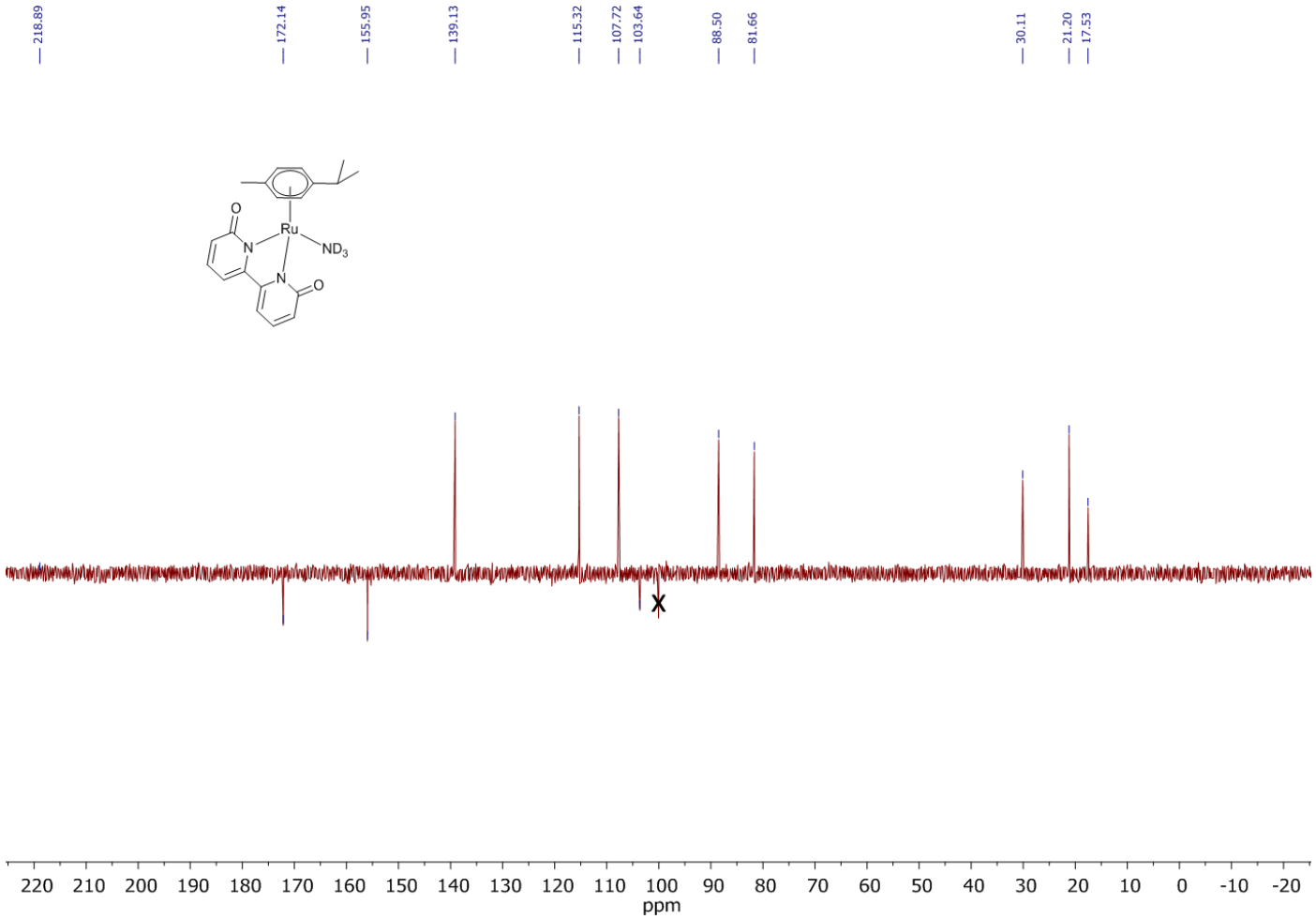


Figure S52. ^{13}C(APT) NMR spectra (75 MHz). 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 20 µL of NH_3 (20% v/v in H_2O). One of the quaternary carbons of p-Cymene is hidden in the background noise of the spectra. Peak at 100 ppm is an artifact (center of the acquisition window).

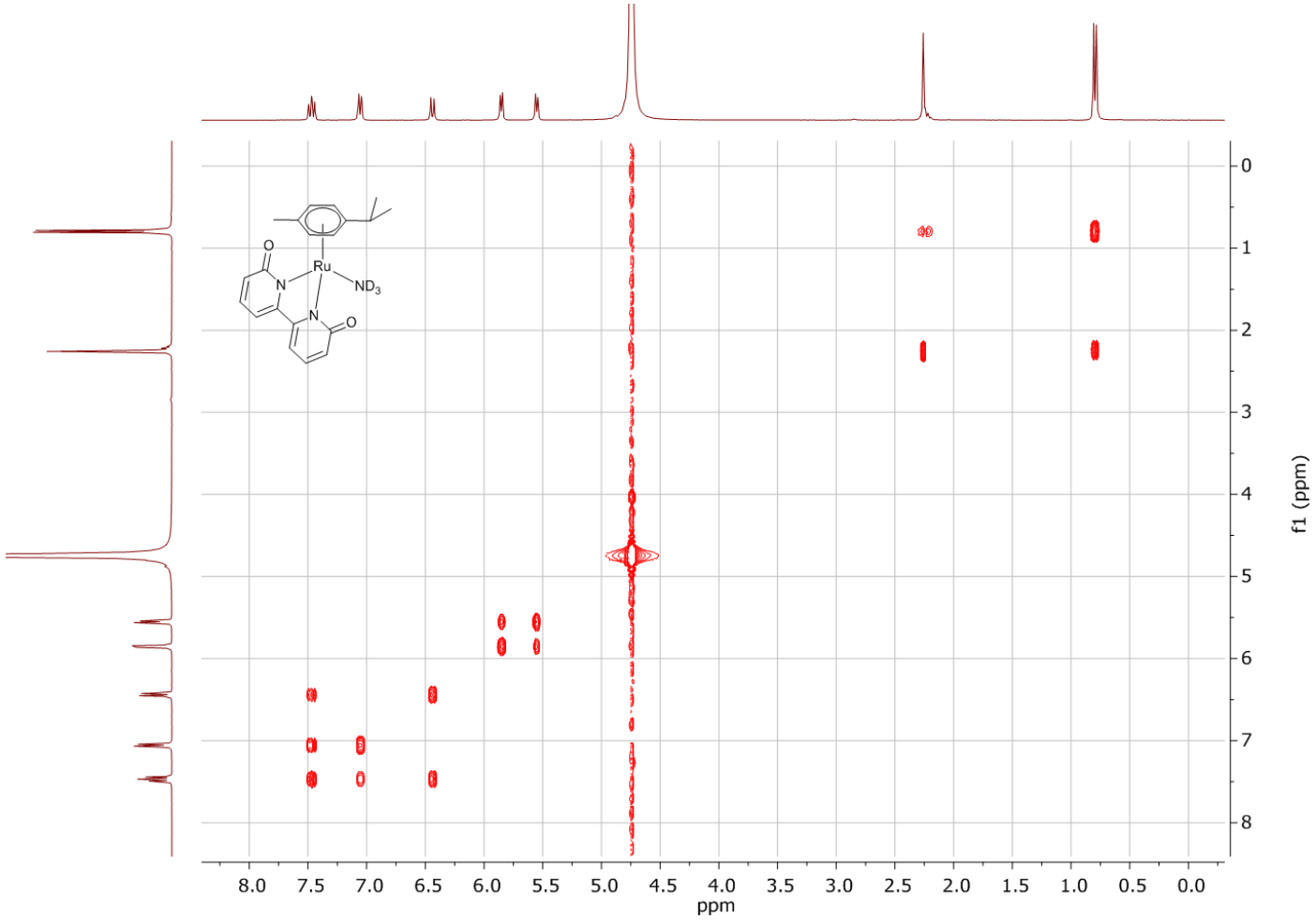


Figure S53. COSY NMR spectra (300 MHz). 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 20 µL of NH_3 (20% v/v in H_2O).

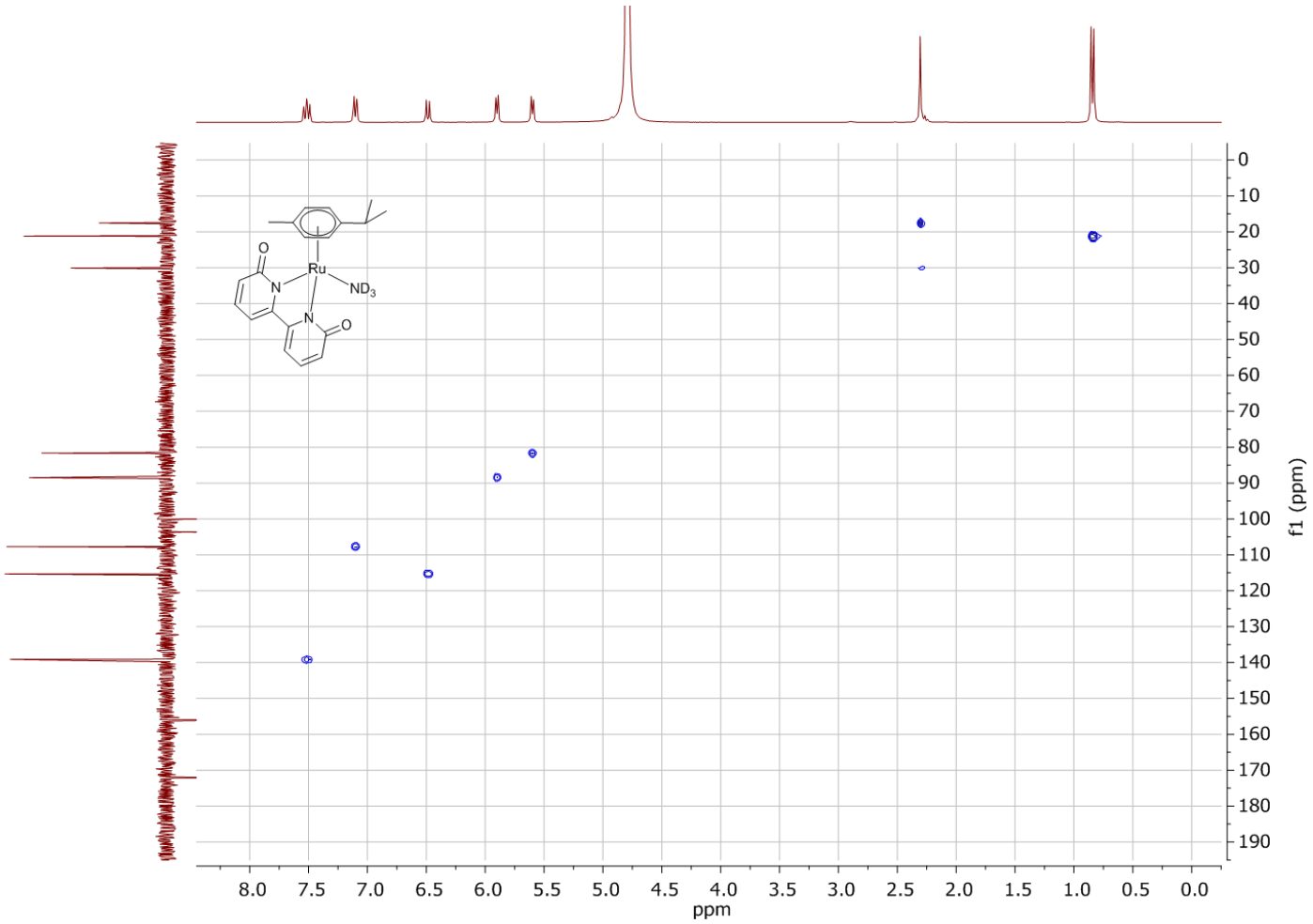


Figure S54. HSQC NMR spectra (300 MHz). 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 20 µL of NH_3 (20% v/v in H_2O).

***In situ* characterization of [Ru(p-Cym)(dhbp-2H)(OD)]$^-$ (0.001 M NaOD/D_2O):**

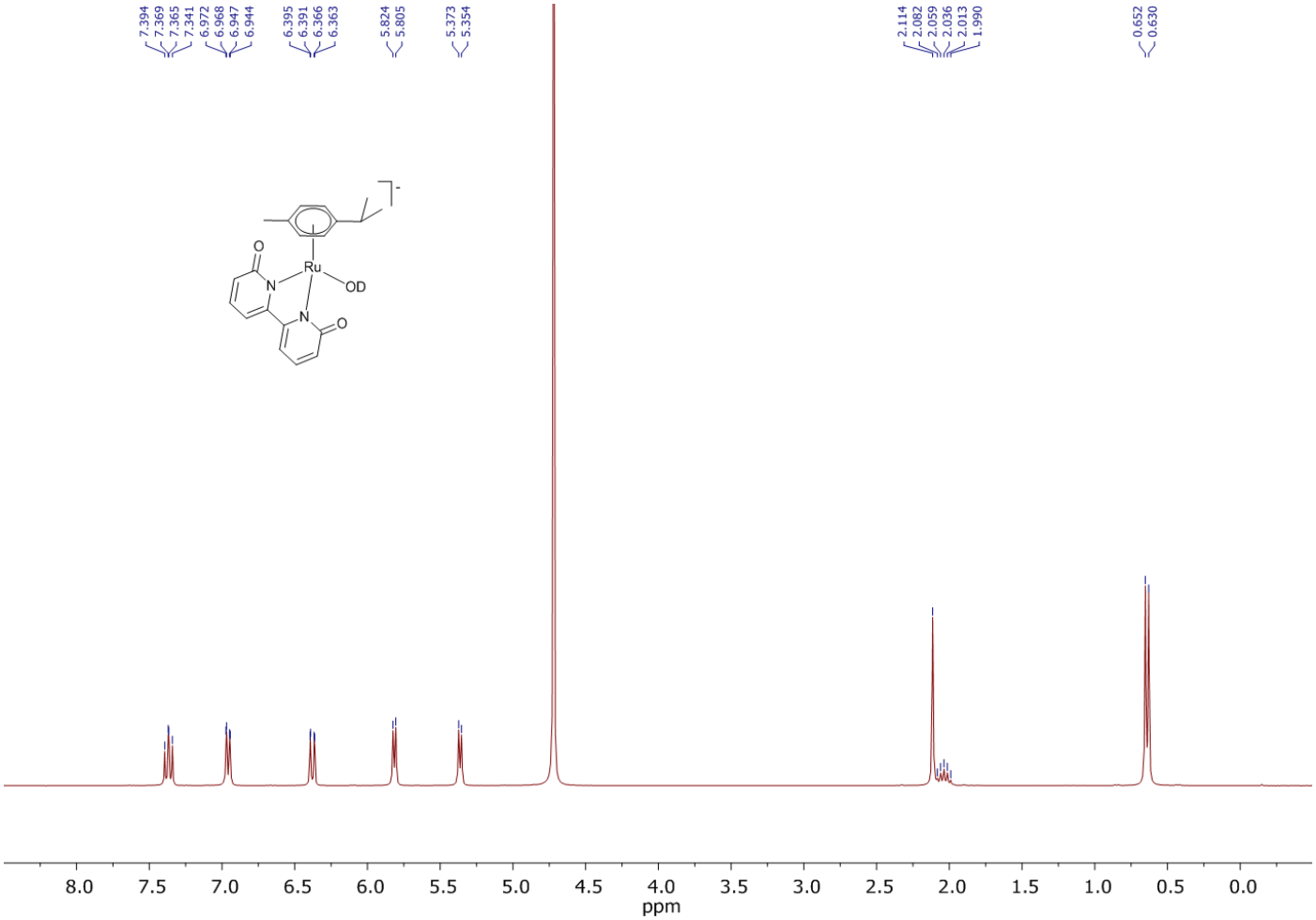


Figure S55. ^{1}H NMR spectra (300 MHz). 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O.

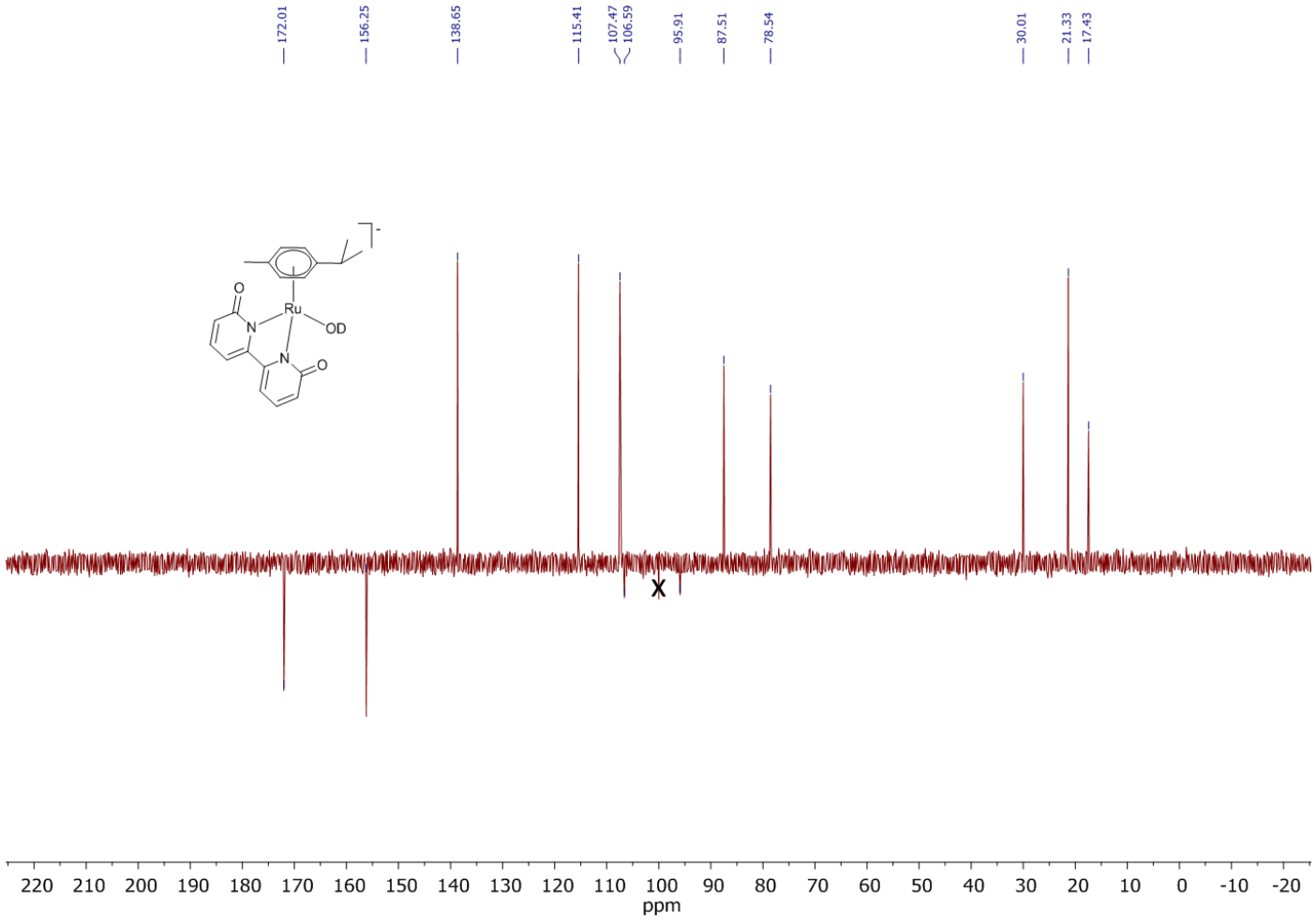


Figure S56. ^{13}C(APT) NMR spectra (75 MHz). 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O. Peak at 100 ppm is an artifact (center of the acquisition window).

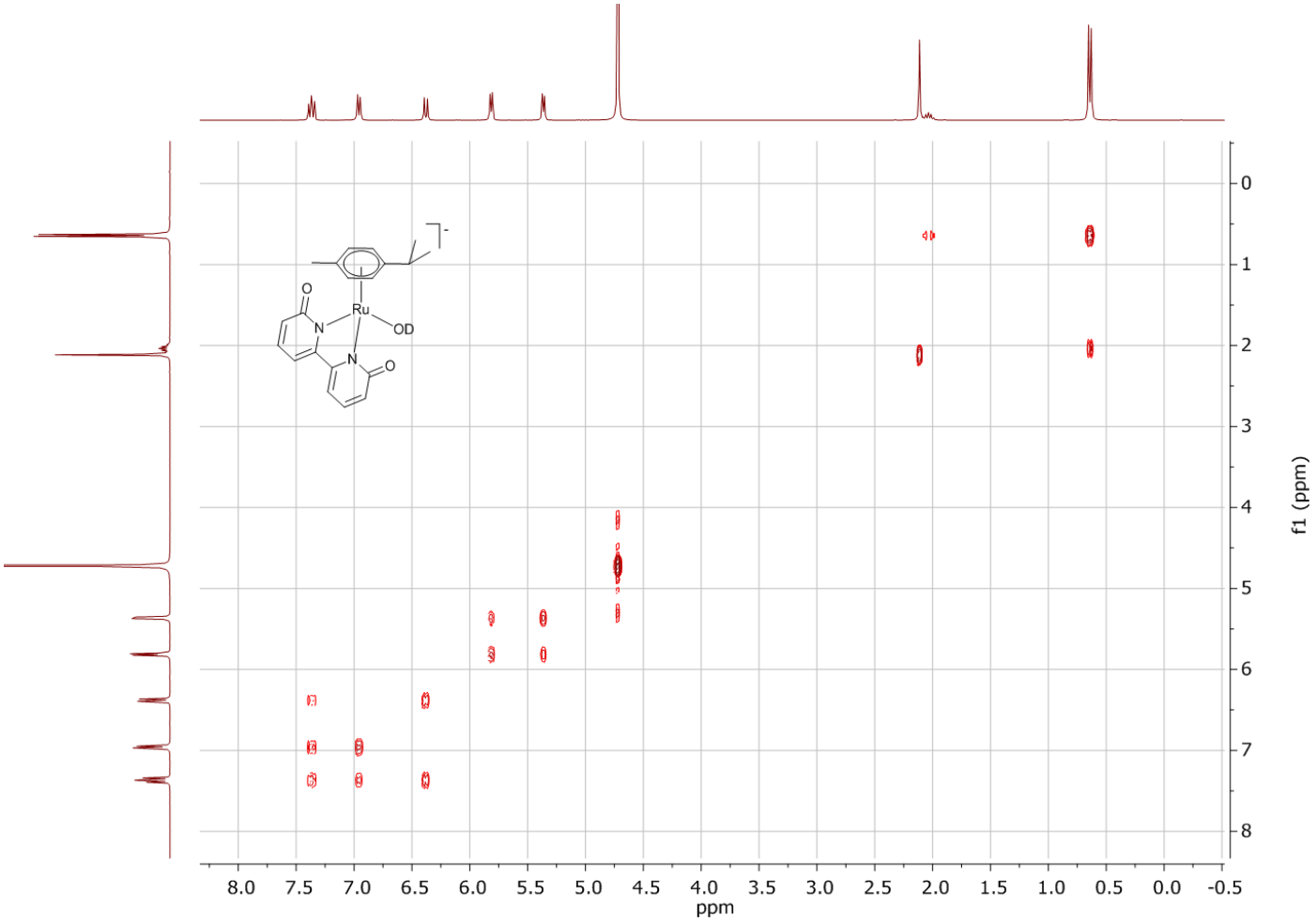


Figure S57. COSY NMR spectra (300 MHz). 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O.

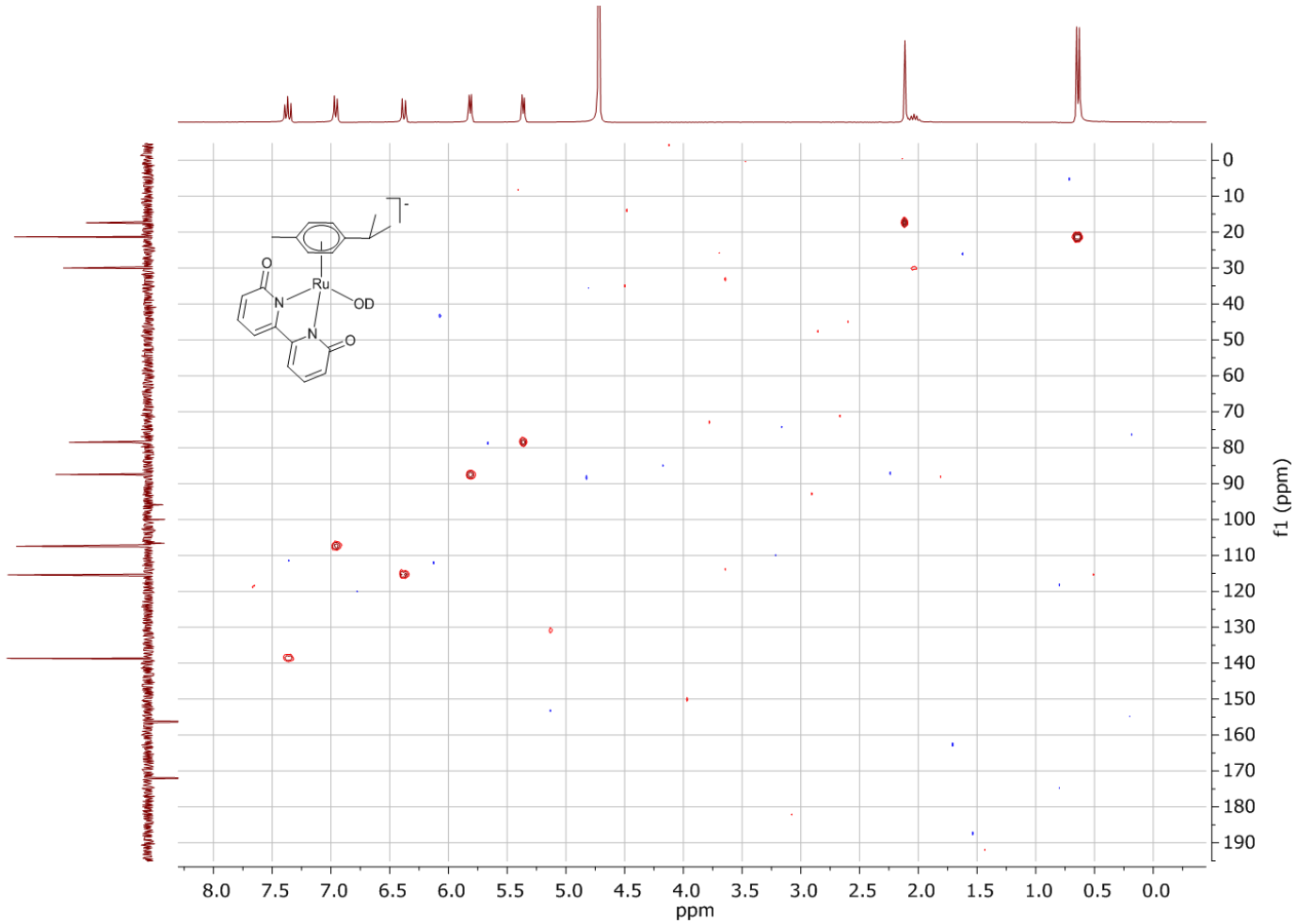
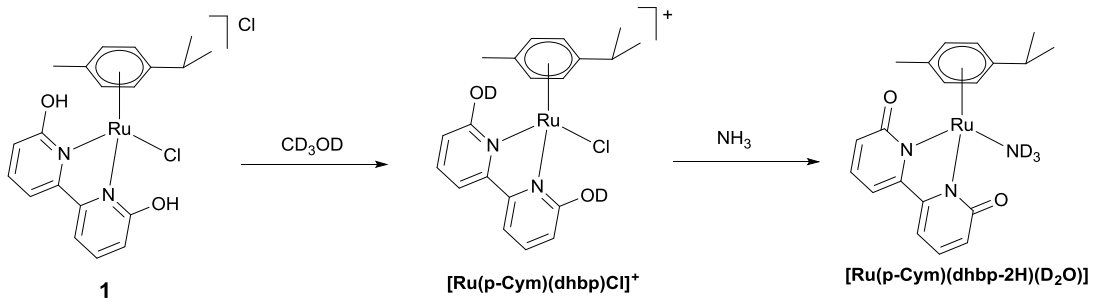


Figure S58. HSQC NMR spectra (300 MHz). 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O.

Scheme S2. Reactivity scheme used for the *in situ* characterizations in CD_3OD:



1 **[Ru(p-Cym)(dhbp)Cl]$^+$** **[Ru(p-Cym)(dhbp-2H)(D_2O)]**

Characterization of [Ru(p-Cym)(dhbp)Cl]Cl (1) in CD_3OD:

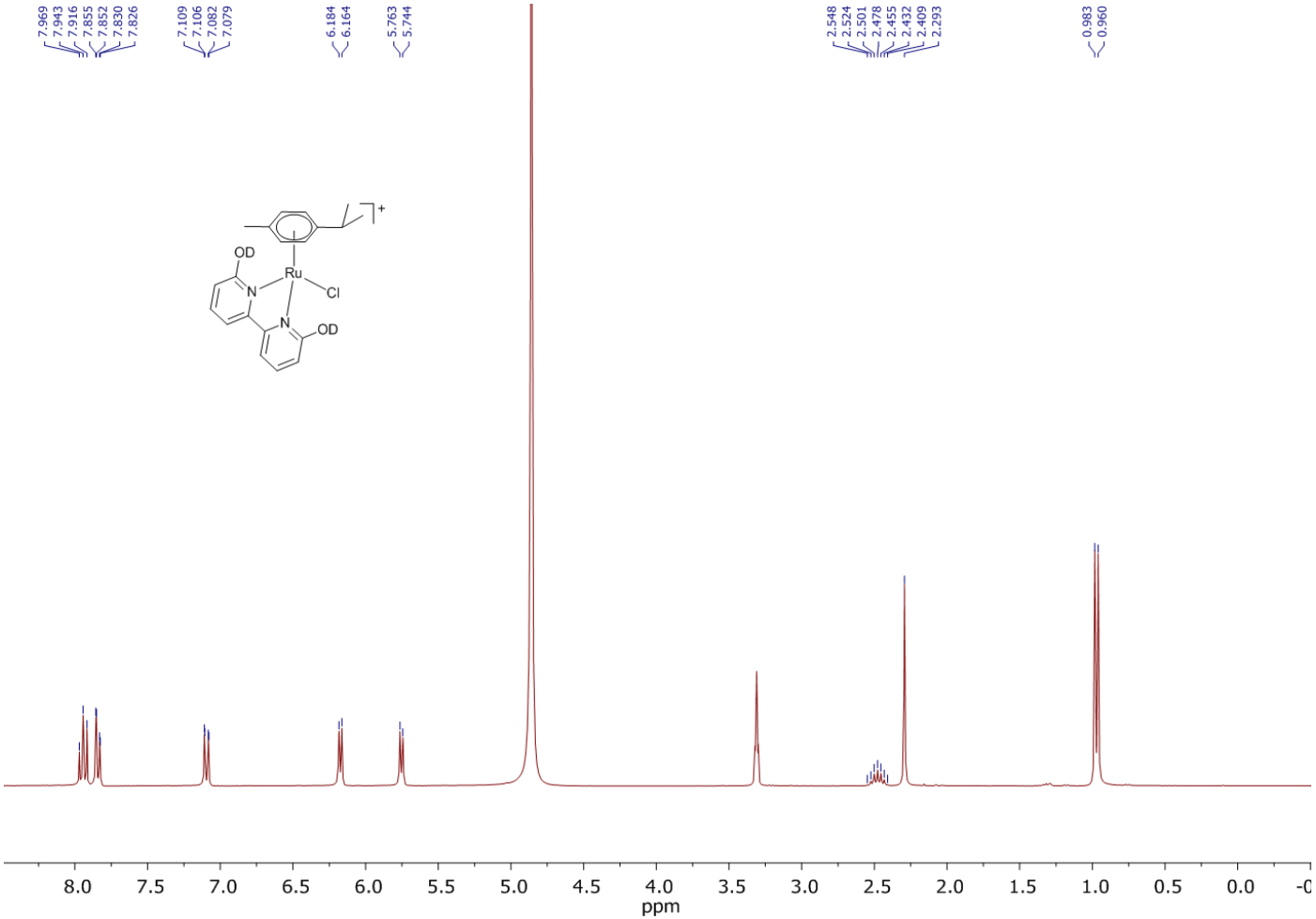


Figure S59 ^{1}H NMR spectra (300 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD.

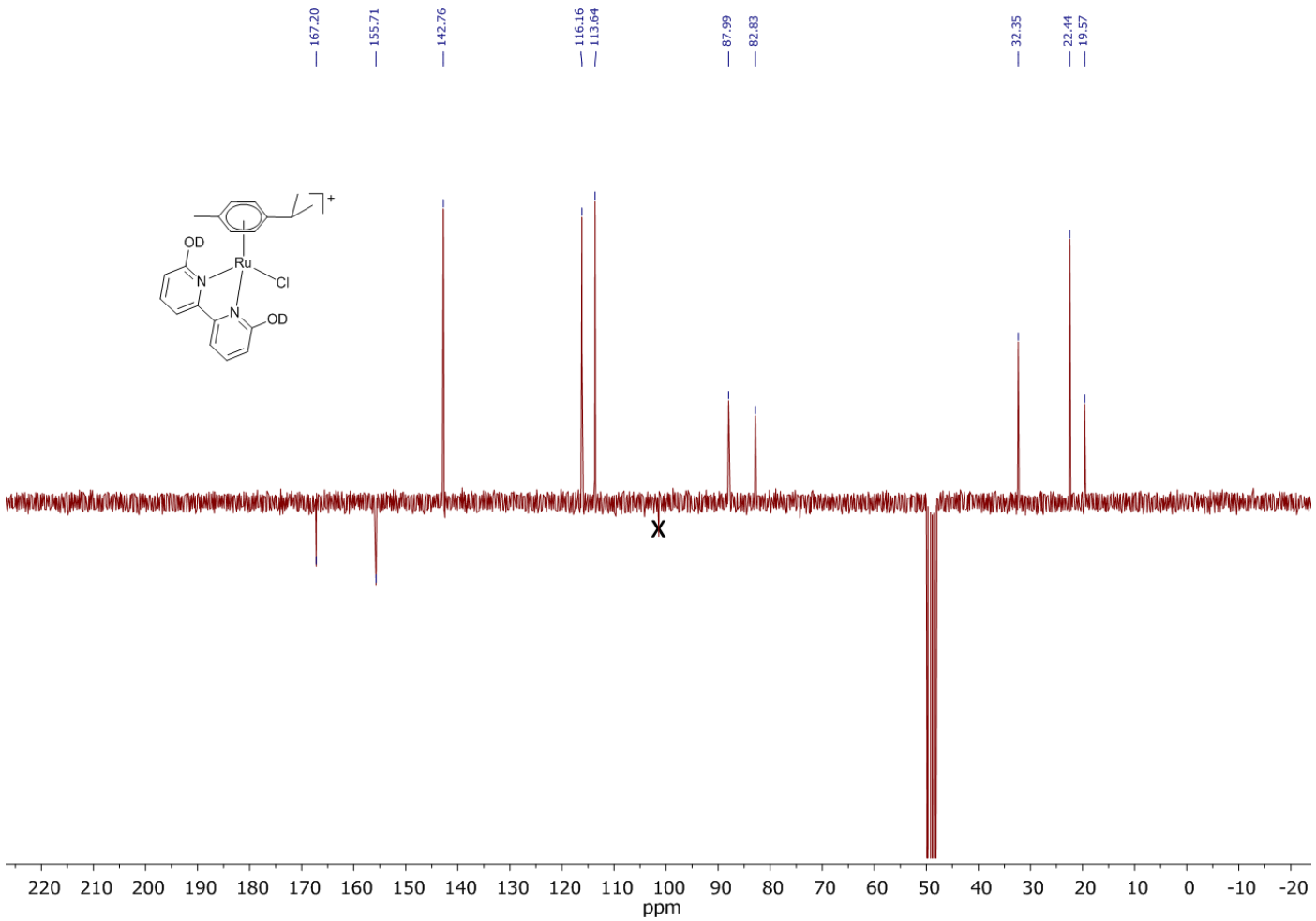


Figure S60. ^{13}C(APT) NMR spectra (75 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD. Quaternary carbons of p-Cymene are hidden in the background noise of the spectra. Peak at 100 ppm is an artifact (center of the acquisition window).

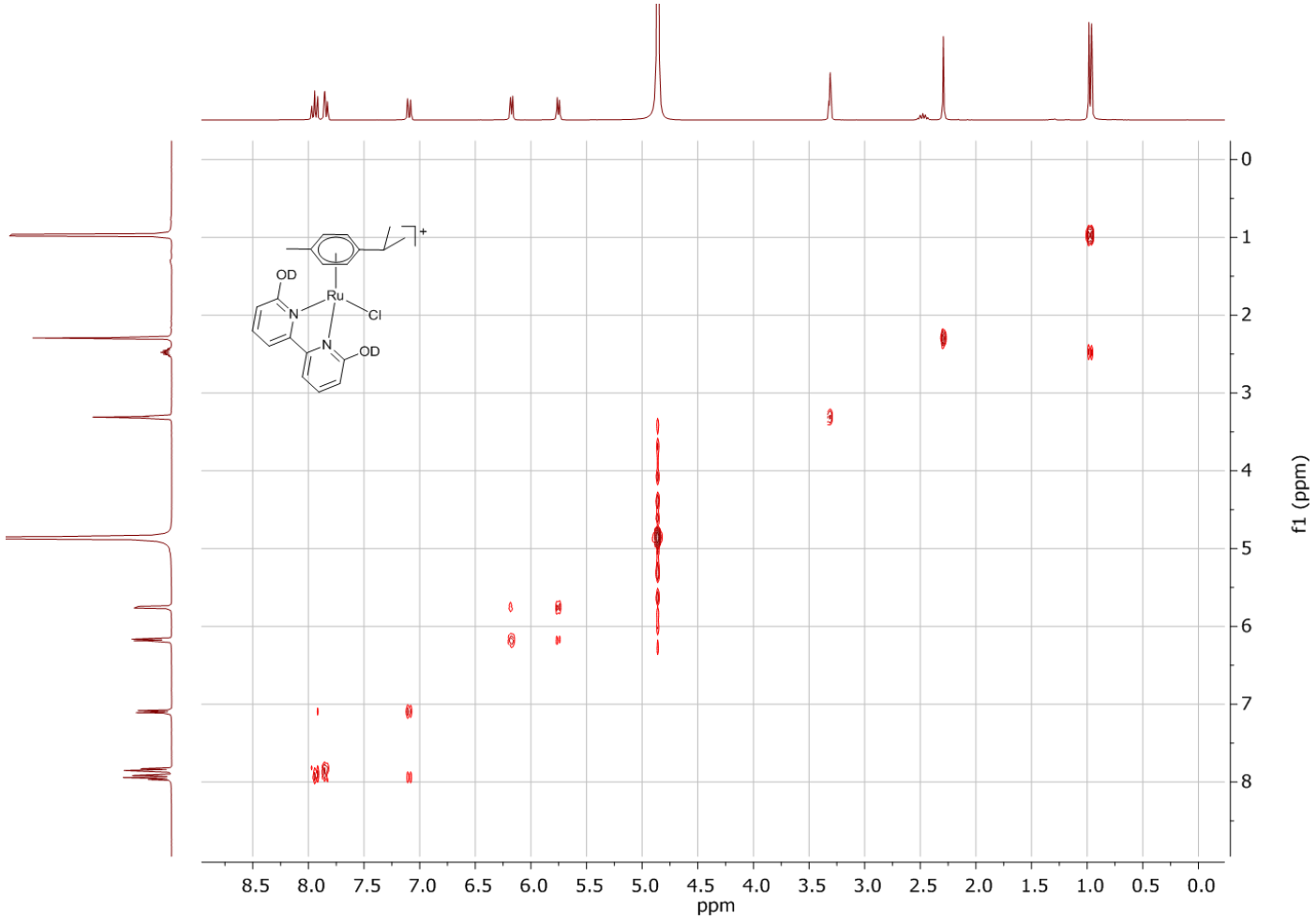


Figure S61. COSY NMR spectra (300 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD.

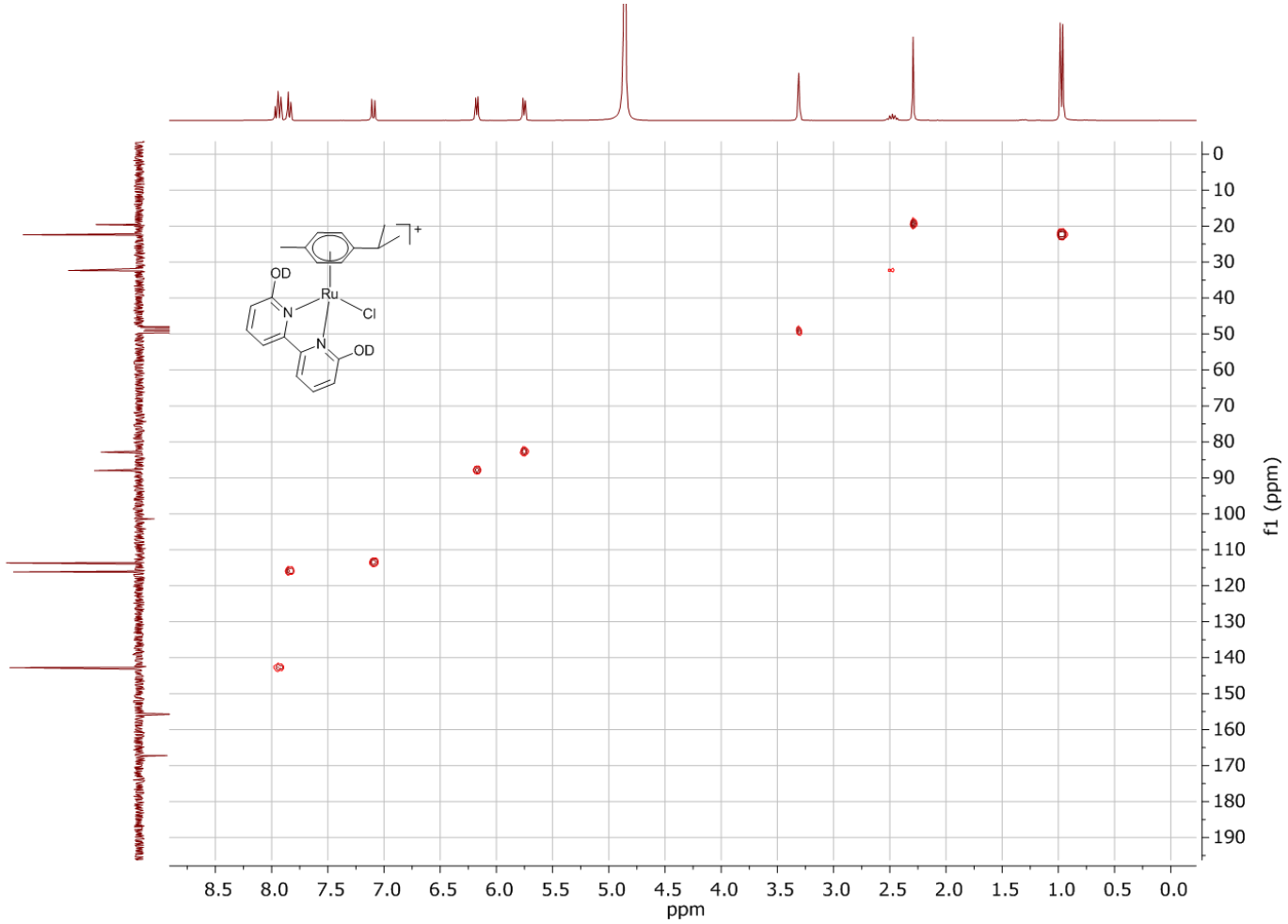


Figure S62. HSQC NMR spectra (300 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD.

***In situ* formation and characterization of [Ru(p-Cym)(dhbp-2H)(ND_3)] (CD_3OD):**

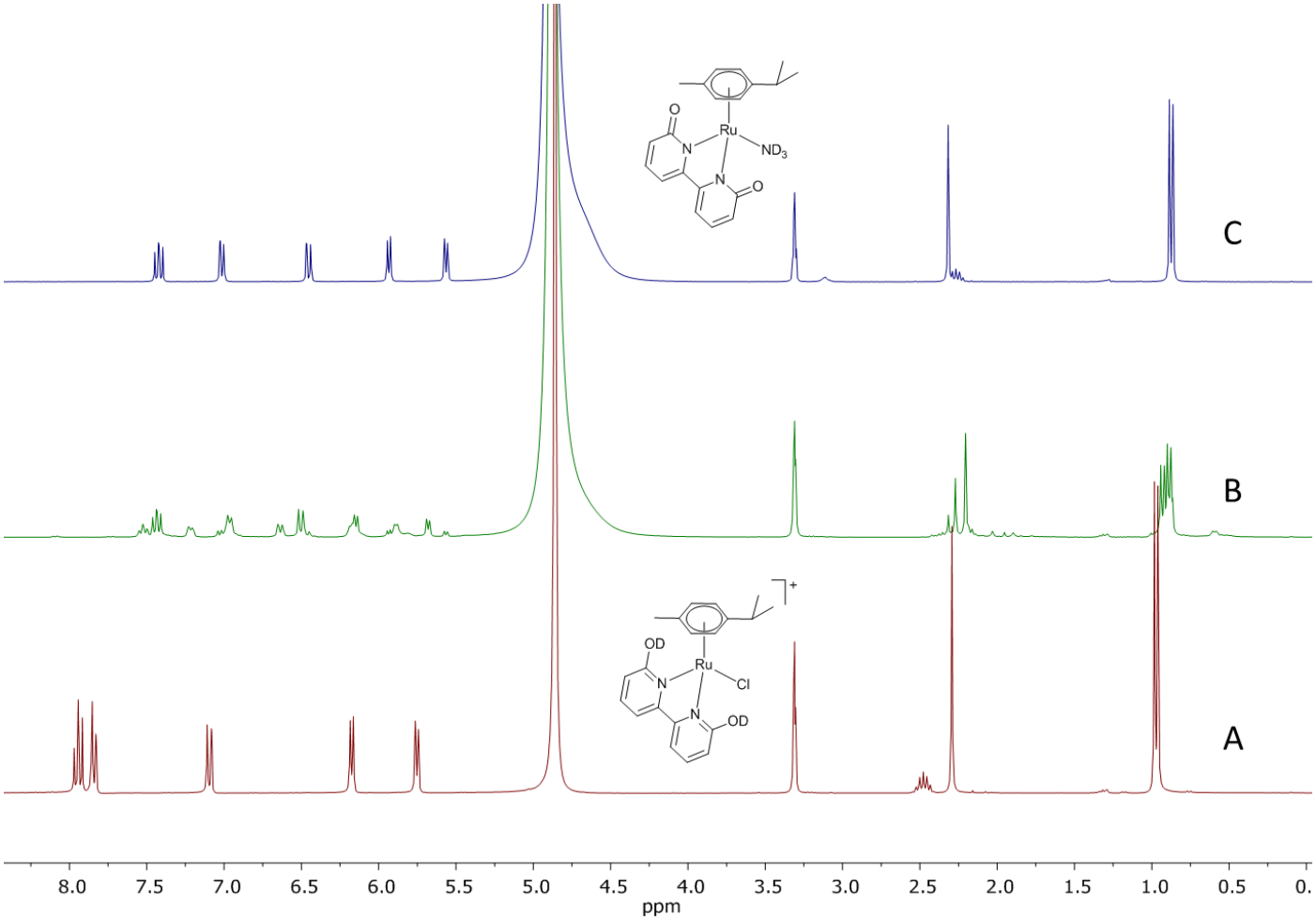


Figure S63.^{1}H NMR spectra (300 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) and in 0.5 mL of CD_3OD. **B:** After addition of 10 µL of NH_3 (20% v/v in H_2O). **B:** After addition of 10 µL more of NH_3 (20% v/v in H_2O).

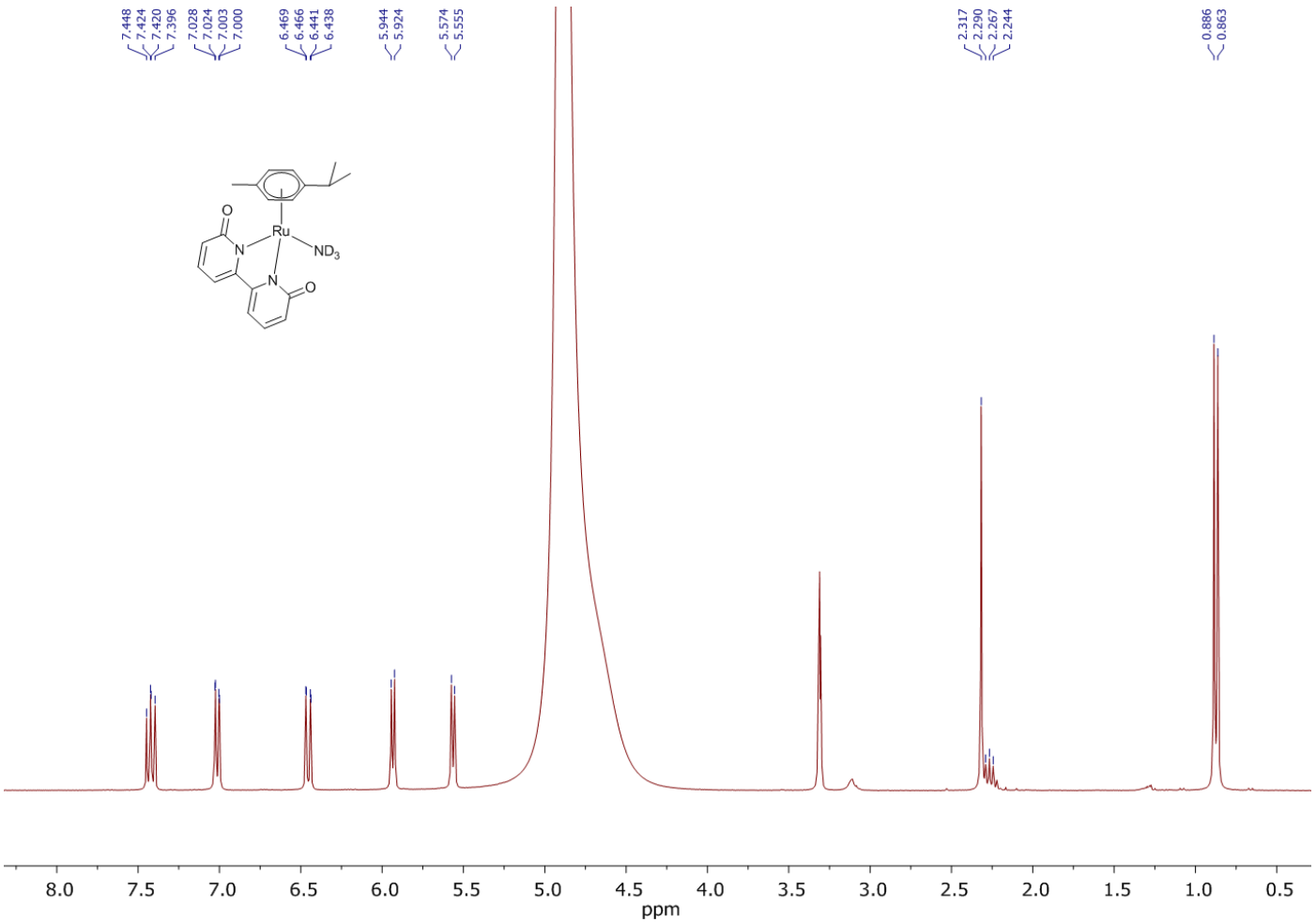


Figure S64. ^{1}H NMR spectra (300 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD, after addition of 20 µL of NH_3 (20% v/v in H_2O).

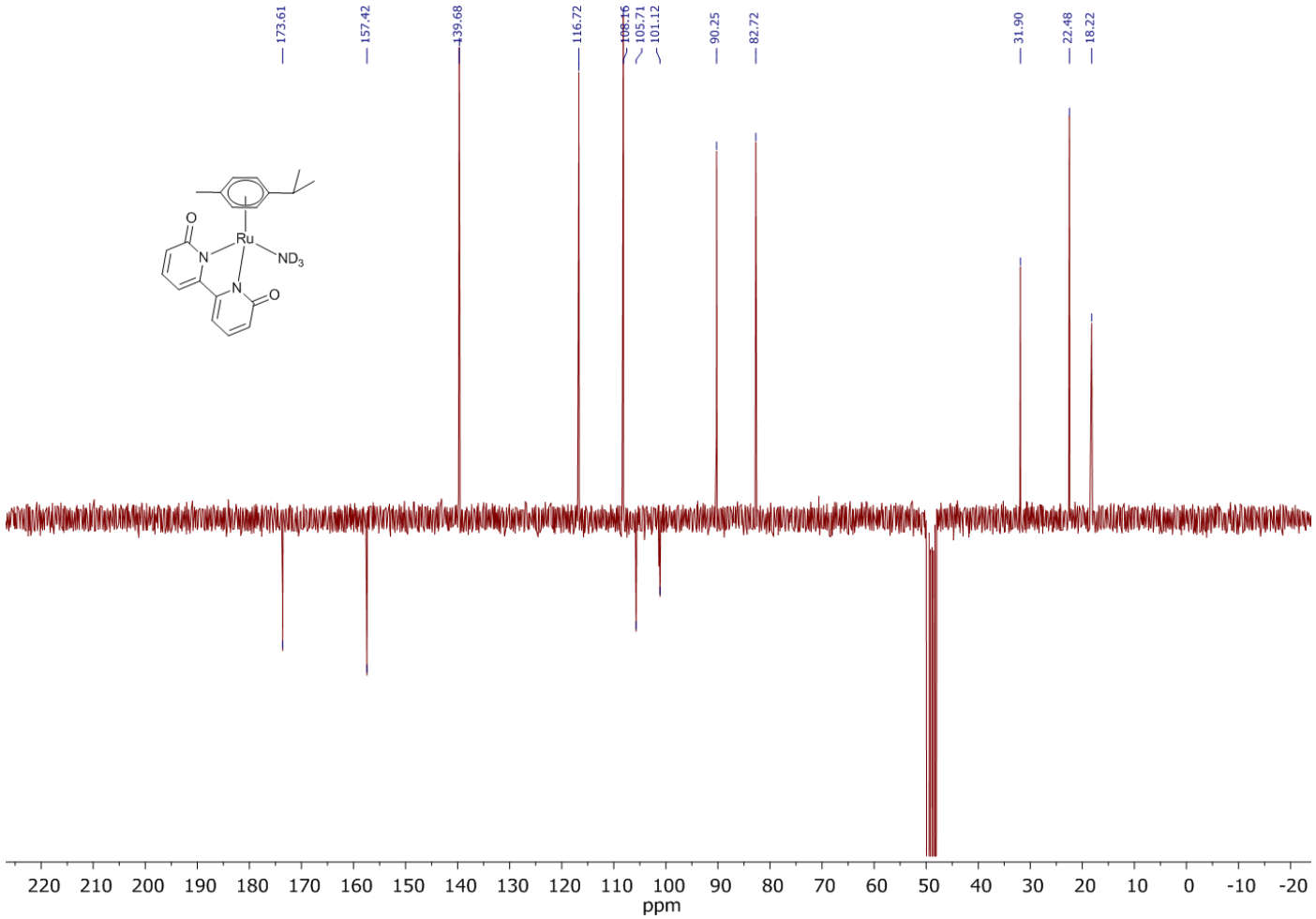


Figure S65. ^{13}C(APT) NMR spectra (75 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD, after addition of 20 µL of NH_3 (20% v/v in H_2O). One of the quaternary carbons of p-Cymene is hidden in the background noise of the spectra. Peak at 100 ppm is an artifact (center of the acquisition window).

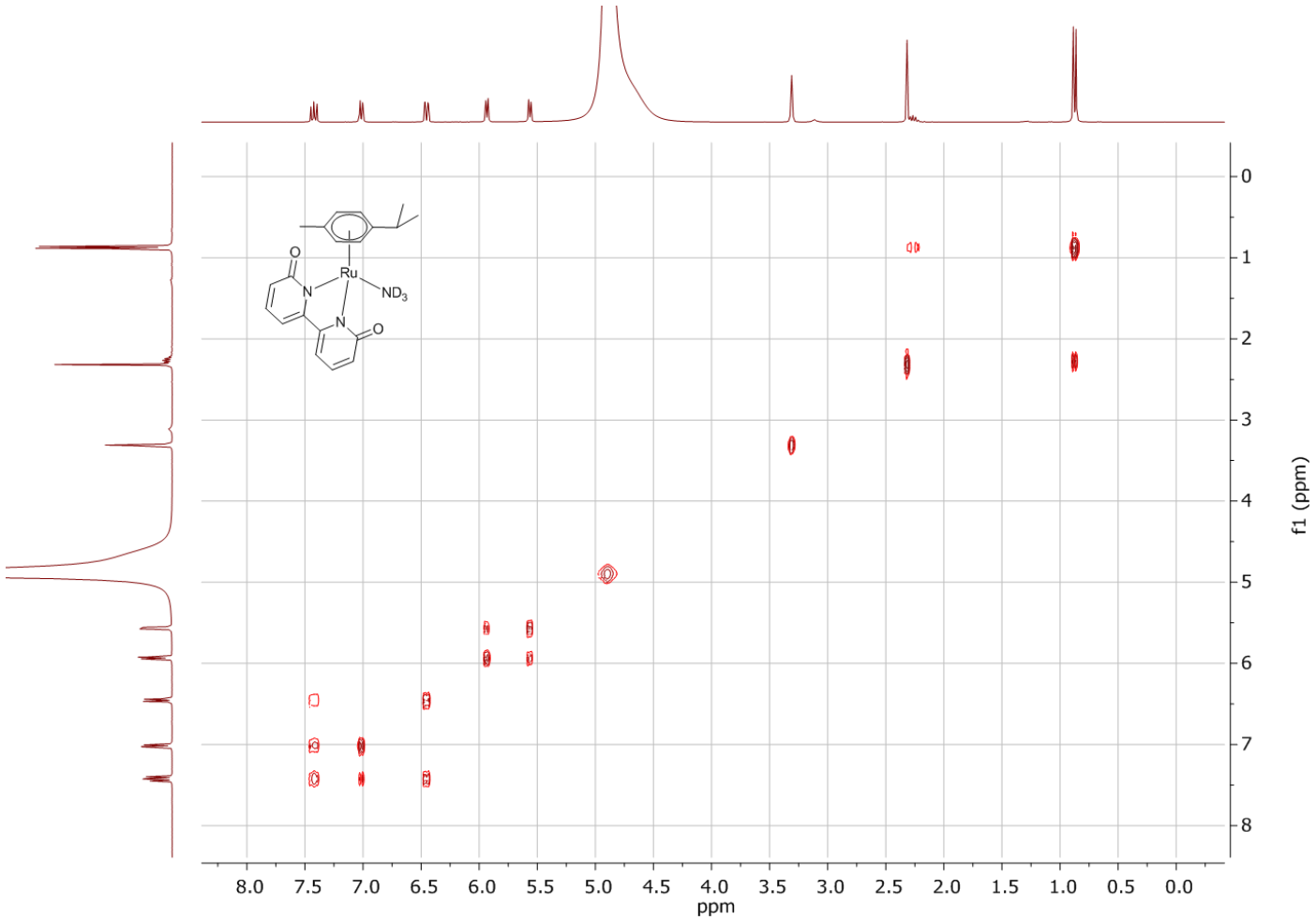


Figure S66. COSY NMR spectra (300 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD, after addition of 20 µL of NH_3 (20% v/v in H_2O).

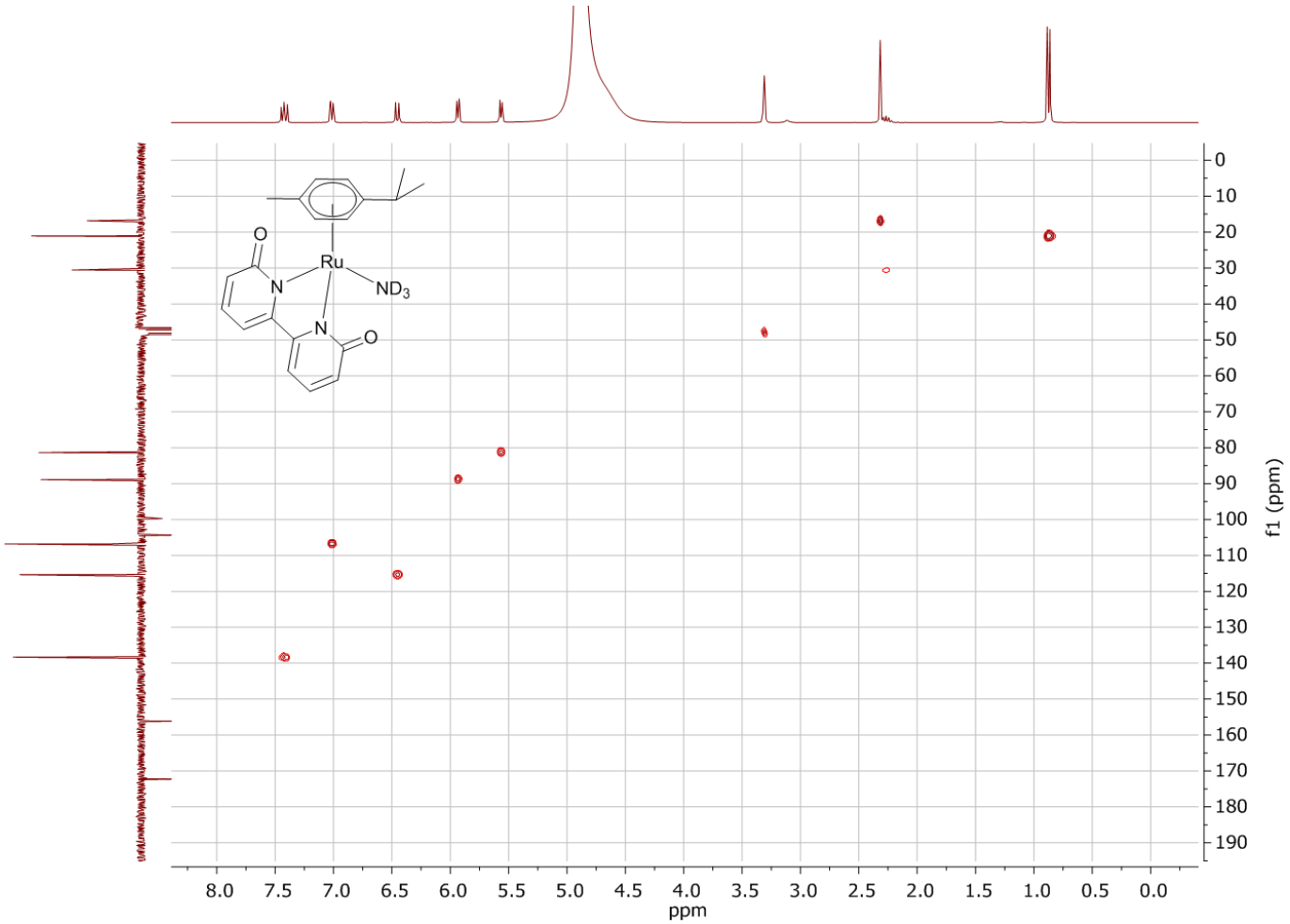


Figure S67. HSQC NMR spectra (300 MHz). 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD, after addition of 20 µL of NH_3 (20% v/v in H_2O).

***In situ* formation and characterization of [Ru(p-Cym)(dhbp-2H)H]$^-$ (0.0001 M NaOD/D_2O):**

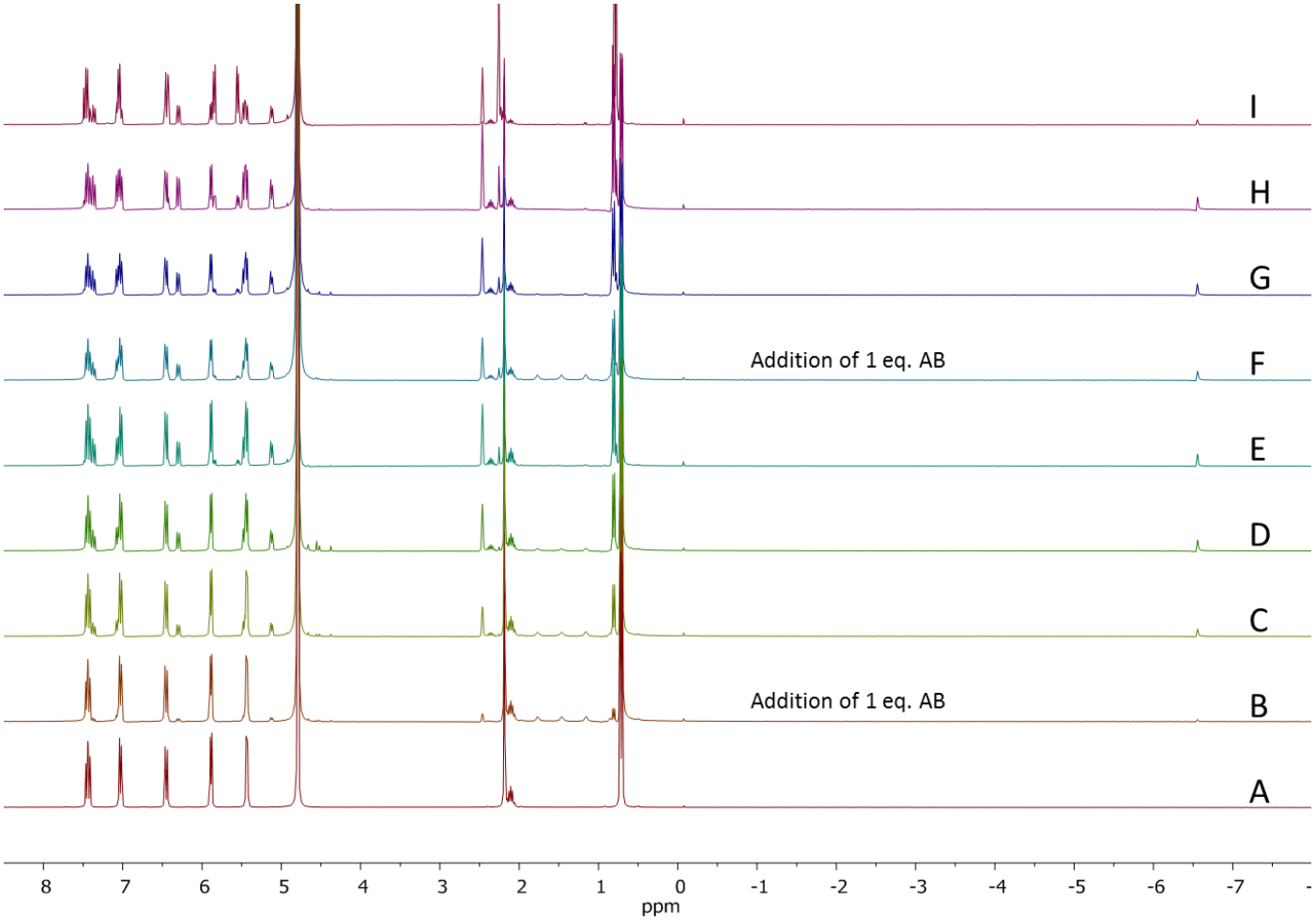


Figure S68.^{1}H NMR spectra (300 MHz, 8.5 to -8.0 ppm) **A:** 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O. **B-E:** Time evolution after addition of 0.25 mg of AB (5 min; 30 min; 60 min; 151 min). **F-I:** Time evolution after addition of another 0.25 mg of AB (2 min; 22 min; 111 min; 1340 min).

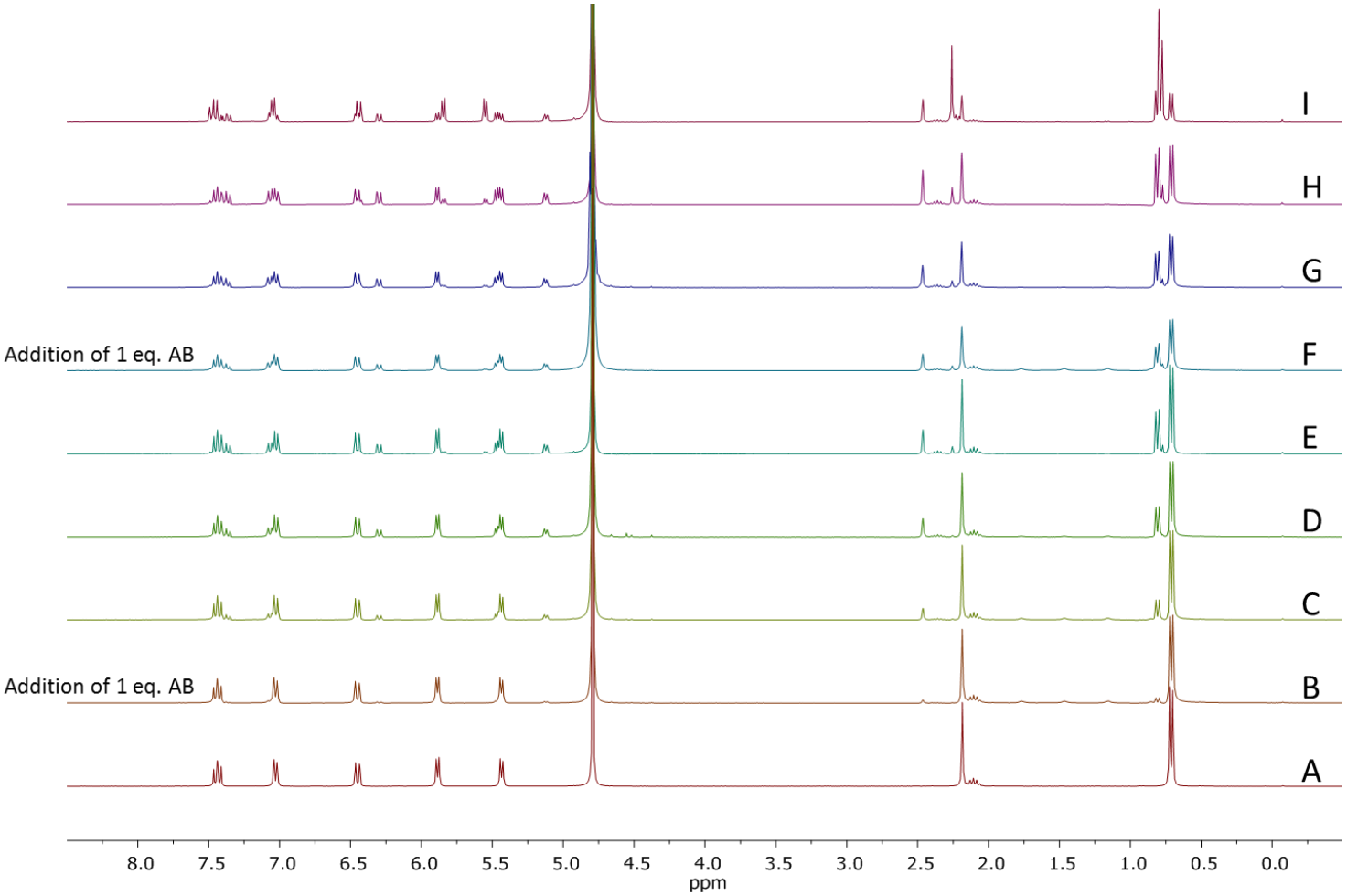


Figure S69. ^{1}H NMR spectra (300 MHz, 8.5 to -0.5 ppm) **A:** 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O. **B-E:** Time evolution after addition of 0.25 mg of AB (5 min; 30 min; 60 min; 151 min). **F-I:** Time evolution after addition of another 0.25 mg of AB (2 min; 22 min; 111 min; 1340 min).

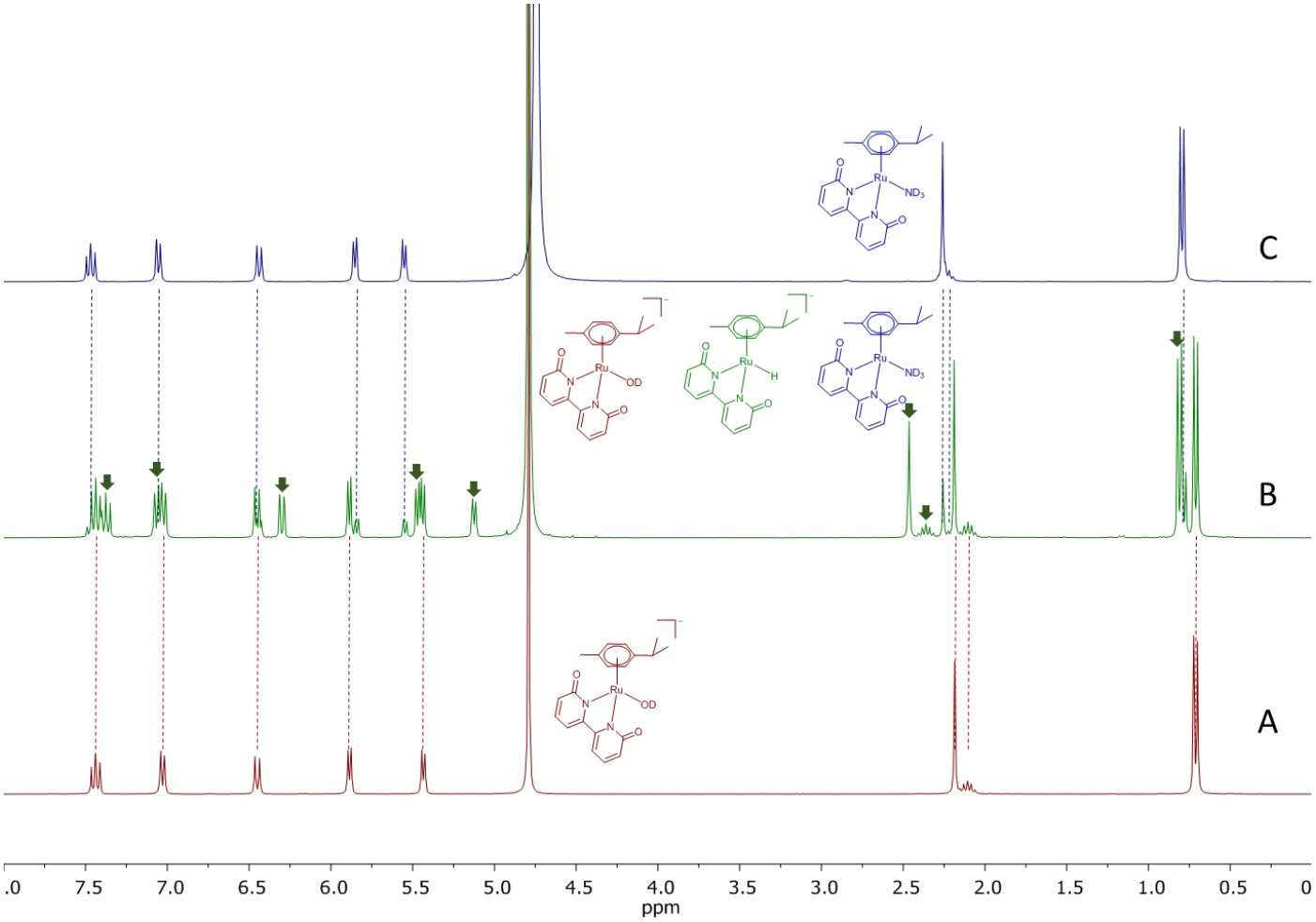


Figure S70. ^{1}H NMR spectra (300 MHz) of **A:** 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O. **B:** 111 min after addition of 2 eq. of AB. **C:** 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 20 µL of NH_3 (20% v/v in H_2O). Signals assigned to $[Ru(p\text{-}Cym)(dhbp\text{-}2H)H]^-$ have been identified with a green arrow.

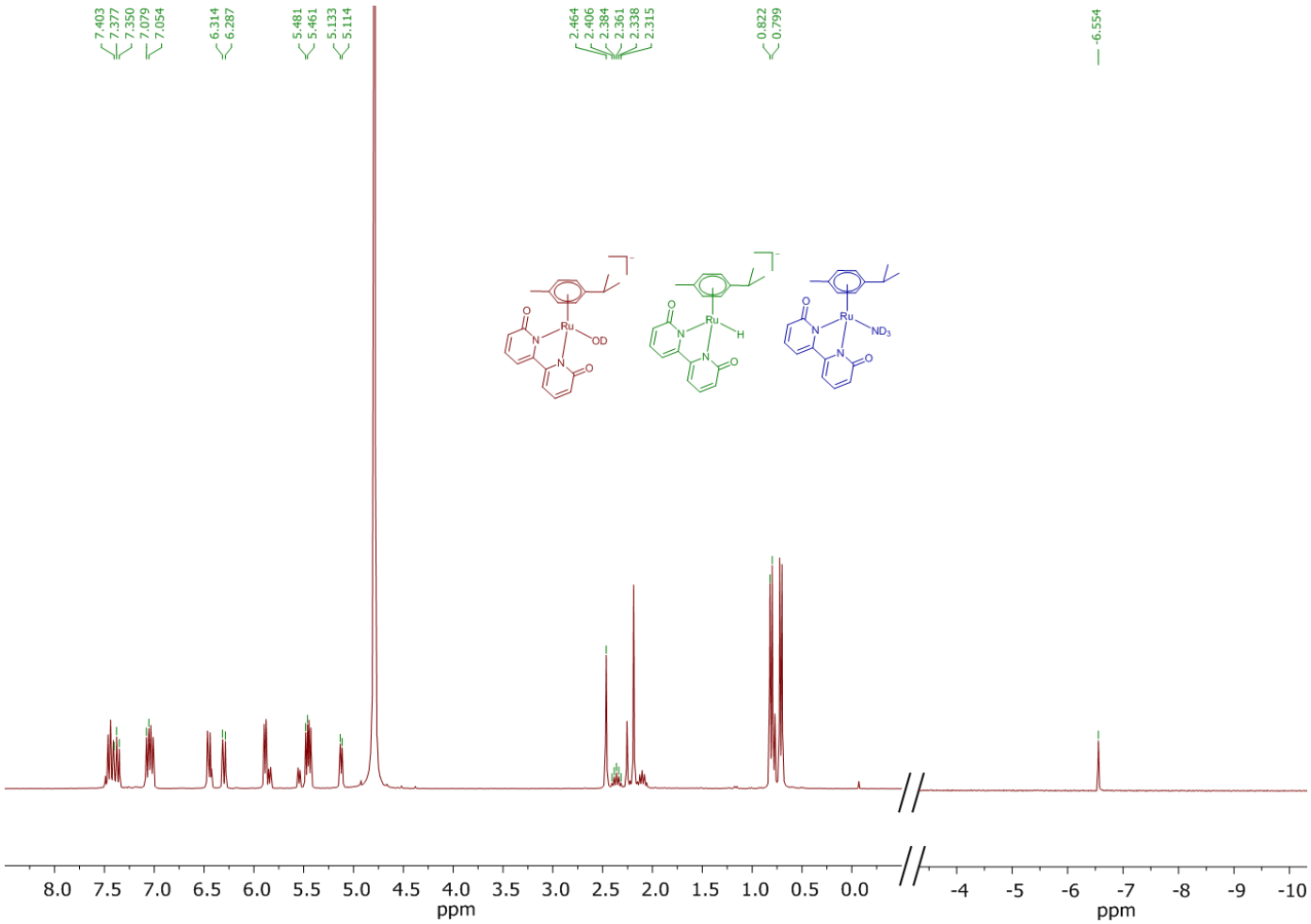


Figure S71. ^{1}H NMR spectra (300 MHz) of 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O, 111 min after addition of 2 eq. of AB. Only signals assigned to $[Ru(p\text{-}Cym)(dhbp\text{-}2H)H]^-$ have been peak-picked.

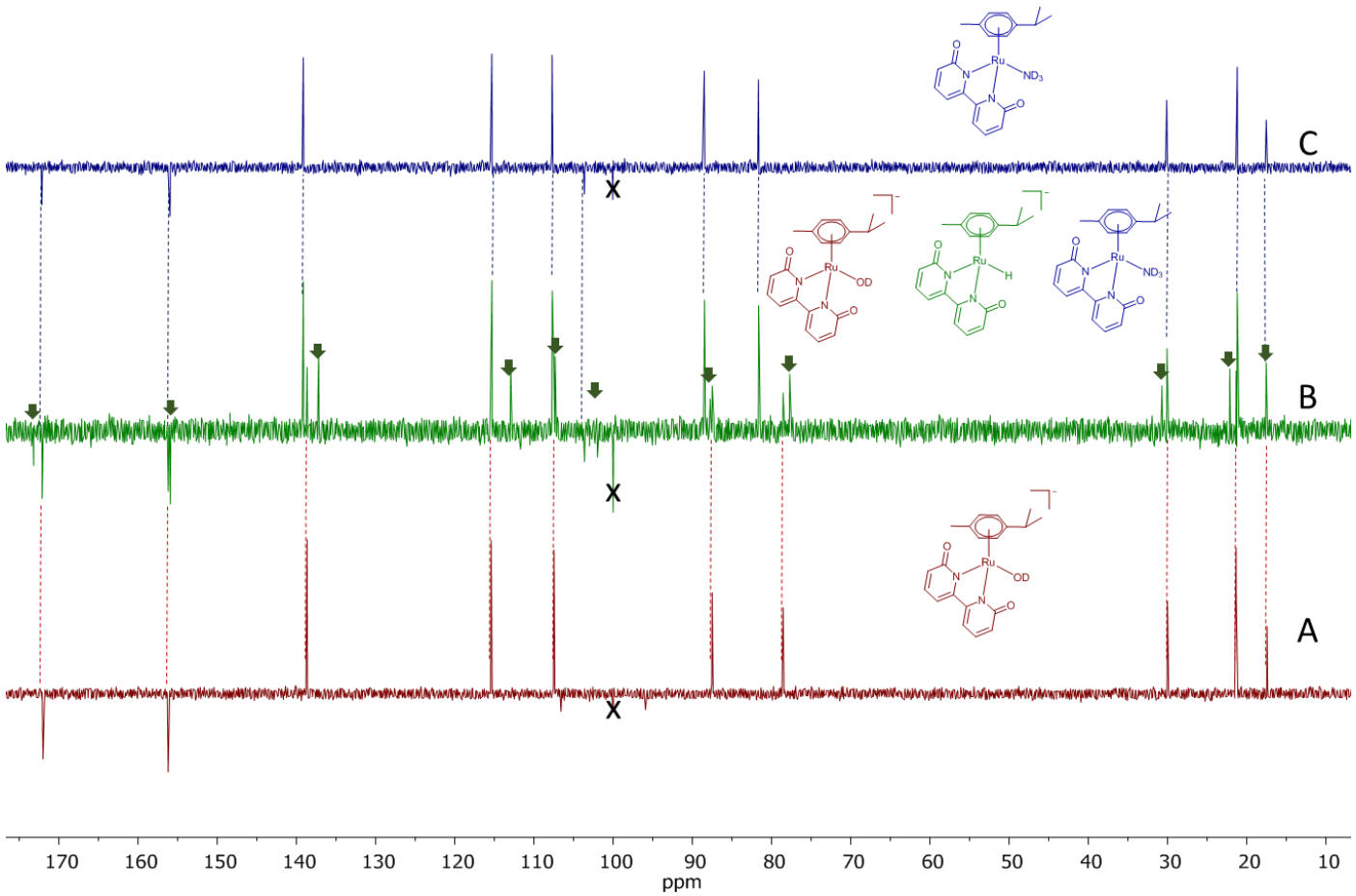


Figure S72. ^{13}C(APT) NMR spectra (75 MHz). **A:** 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O. **B:** 111 min after addition of 2 eq. of AB. **C:** 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O, after addition of 20 µL of NH_3 (20% v/v in H_2O). Signals assigned to $[Ru(p\text{-}Cym)(dhbp\text{-}2H)H]^-$ have been identified with a green arrow. Peak at 100 ppm is an artifact (center of the acquisition window).

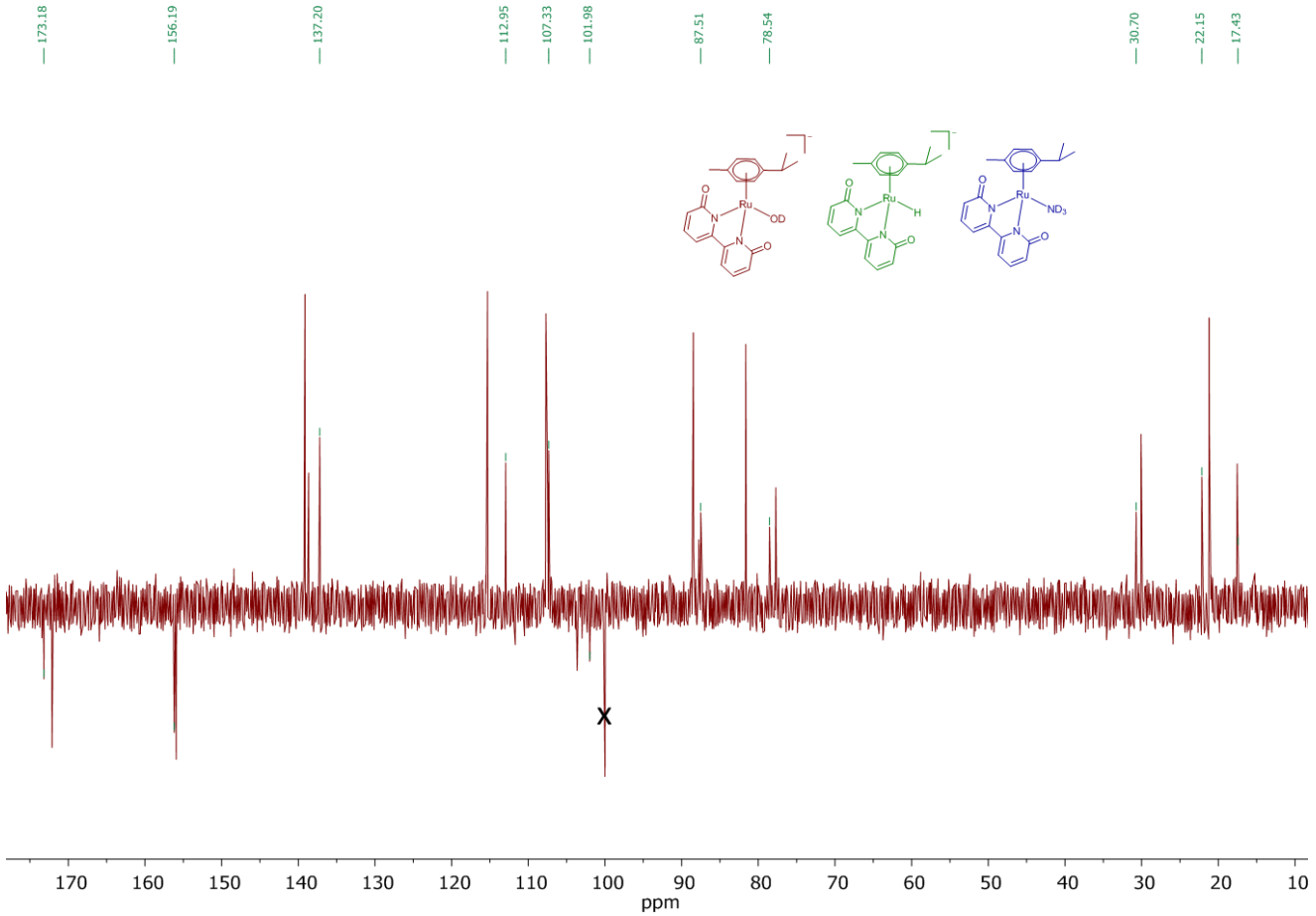


Figure S73. ^{13}C(APT) NMR spectra (75 MHz). **A:** 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O, 111 min after addition of 2 eq. of AB. Signals assigned to $[Ru(p\text{-}Cym)(dhbp\text{-}2H)H]^-$ have been identified with a green arrow. Only signals assigned to $[Ru(p\text{-}Cym)(dhbp\text{-}2H)H]^-$ have been peak-picked.One of the quaternary carbons of p-Cymene is hidden in the background noise of the spectra. Peak at 100 ppm is an artifact (center of the acquisition window).

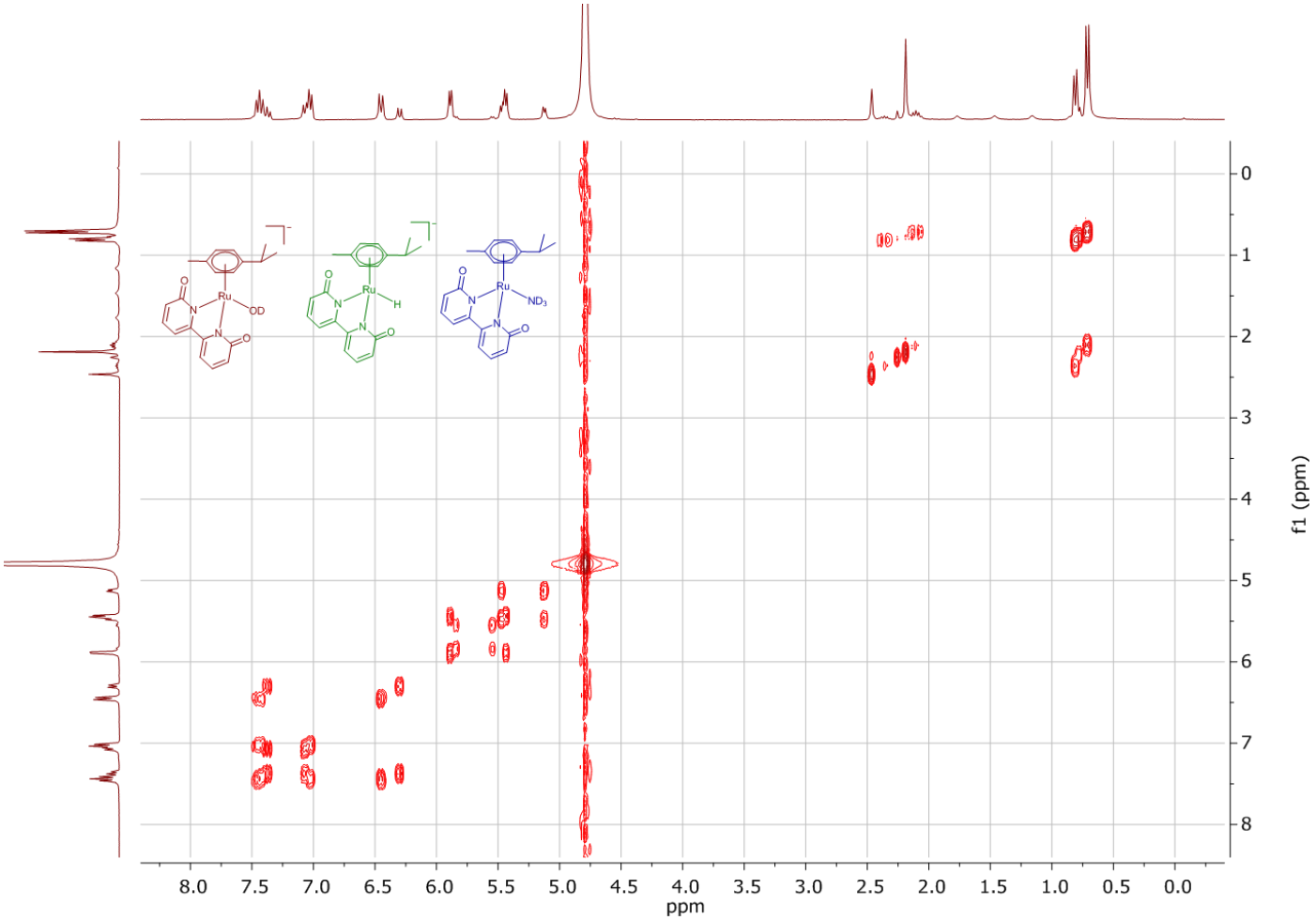


Figure S74. COSY NMR spectra (300 MHz). 4.03 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of 0.001 M NaOD in D_2O, after addition of 2 eq. of AB.

Table S2. ^{1}H NMR chemical shift data (ppm) of $[Ru(pCym)(dhbp)L]^{n+}$ and $[Ru(pCym)(dhbp\text{-}2H)L]^{n-}$ generated *in situ*.

Comp.	H_{Ar1}	H_{Ar2}	H_{Ar3}	H_{pCym1}	H_{pCym2}	CH_{iPr}	CH_3	iPr	solvent
$[Ru(p\text{-}Cym)(dhpb)(D_2O)]^{2+}$	8.01	7.79	7.20	6.30	6.04	2.31	2.24	0.88	D_2O
$[Ru(p\text{-}Cym)(dhpb)Cl]^{+}$	7.98	7.83	7.19	6.23	5.83	2.38	2.27	0.89	D_2O
	7.94	7.84	7.09	6.17	5.75	2.48	2.29	0.97	CD_3OD
$[Ru(p\text{-}Cym)(dhpb\text{-}2H)(D_2O)]$									
$[Ru(p\text{-}Cym)(dhpb\text{-}2H)(ND_3)]$	7.47	7.05	6.44	5.85	5.54	2.22	2.26	0.79	D_2O
	7.42	7.01	6.45	5.93	5.56	2.27	2.32	0.87	CD_3OD
$[Ru(p\text{-}Cym)(dhpb\text{-}2H)(OD)]^{-}$	7.37	6.96	6.38	5.81	5.37	2.04	2.11	0.67	$NaOD/D_2O$
$[Ru(p\text{-}Cym)(dhpb\text{-}2H)H]^{-}$	7.31	7.03	6.47	5.66	5.24	2.56	2.49	1.03	CD_3OD
	7.38	7.07	6.30	5.48	5.12	2.36	2.46	0.81	$NaOD/D_2O$

Spectra description:

Ru–H_2O ($[Ru(p\text{-}Cym)(dhpb)(D_2O)]^{2+}$) ^{1}H NMR (300 MHz, D_2O) δ 8.01 (t, J = 8 Hz, 2H), 7.79 (dd, J = 7.8, 1.0 Hz, 2H), 7.20 (dd, J = 8.5, 0.9 Hz, 2H), 6.30 (d, J = 6.2 Hz, 2H), 6.04 (d, J = 6.0 Hz, 2H), 2.31 (hept, J = 7.20 Hz, 1H), 2.24 (s, 3H), 0.88 (d, J = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, D_2O) δ 165.80, 154.28, 142.76, 115.23, 113.10, 105.57, 97.05, 87.30, 82.29, 30.13, 20.97, 17.77. [119.60 (q, J = 317.2 Hz, $O_3SCF_3^-$)]

Ru–Cl ($[Ru(p\text{-}Cym)(dhpb)Cl]^{+}$) ^{1}H NMR (300 MHz, D_2O) δ 7.98 (t, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.23 (d, *J* = 5.9 Hz, 2H), 5.83 (d, *J* = 5.9 Hz, 4H), 2.38 (hept, *J* = 7.0 Hz, 1H), 2.27 (s, 3H), 0.89 (d, *J* = 6.9 Hz, 9H). ^{13}C NMR (75 MHz, D2O) δ 165.22, 153.86, 142.19, 115.70, 112.83, 87.29, 81.93, 30.46, 21.23 (quaternary carbons of p-Cym not observed).

Ru–Cl ($[Ru(p\text{-}Cym)(dhpb)Cl]^{+}$) ^{1}H NMR (300 MHz, CD_3OD) δ 7.94 (t, *J* = 8.0 Hz, 2H), 7.84(dd, *J* = 7.7, 1.2 Hz, 2H), 7.09 (dd, *J* = 8.1, 1.1 Hz, 2H), 6.17 (d, *J* = 6.0 Hz, 2H), 5.75 (d, *J* = 5.9 Hz, 2H), 2.48 (hept, *J* = 6.9 Hz, 1H), 2.29 (s, 3H), 0.97 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, CD_3OD) δ 167.20, 155.71, 142.76, 116.16, 113.64, 87.99, 82.83, 32.35, 22.44, 19.57 (quaternary carbons of p-Cym not observed).

Ru–NH_3 ($[Ru(p\text{-}Cym)(dhpb\text{-}2H)(ND_3)]$) ^{1}H NMR (300 MHz, D_2O) δ 7.47 (dd, *J* = 8.5, 7.3 Hz, 2H), 7.05 (dd, *J* = 7.4, 1.1 Hz, 2H), 6.44 (dd, *J* = 8.5, 1.0 Hz, 2H), 5.85 (d, *J* = 5.9 Hz, 2H), 5.54 (d, *J* = 6.0 Hz, 2H), 2.26 (s, 3H), 2.22 (hept, *J* = 7.0 Hz, 1H), 0.79 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, D_2O) δ 218.89, 172.14, 155.95, 139.13, 115.32, 107.72, 103.64, 88.50, 81.66, 30.11, 21.20, 17.53.

Ru–NH_3 ($[Ru(p\text{-}Cym)(dhpb\text{-}2H)(ND_3)]$) ^{1}H NMR (300 MHz, CD_3OD) δ 7.42 (dd, *J* = 8.4, 7.3 Hz, 2H), 7.01 (dd, *J* = 7.3, 0.9 Hz, 2H), 6.45 (dd, *J* = 8.5, 0.9 Hz, 2H), 5.93 (d, *J* = 6.0 Hz, 2H), 5.56 (d, *J* = 6.0 Hz, 2H), 2.32 (s, 3H), 2.27 (hept, *J* = 7.0 Hz, 1H), 0.87 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, CD_3OD) δ 173.61, 157.42, 139.68, 116.72, 108.16, 105.71, 101.12, 90.25, 82.72, 31.90, 22.48, 18.22.

Ru–OD ($[Ru(p\text{-}Cym)(dhpb\text{-}2H)(OD)]^{-}$) ^{1}H NMR (300 MHz, 300 MHz, NaOD in D_2O, 0.001 M). δ 7.37 (dd, *J* = 8.4, 7.3 Hz, 2H), 6.96 (dd, *J* = 7.5, 1.2 Hz, 2H), 6.38 (dd, *J* = 8.5, 1.1 Hz, 2H), 5.81 (d, *J* = 5.8 Hz, 2H), 5.37 (d, *J* = 5.7 Hz, 2H), 2.11 (s, 3H), 2.04 (hept, *J* = 6.8 Hz, 1H), 0.67 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, NaOD in D_2O, 0.001 M) δ 172.01, 156.25, 138.65, 115.41, 107.47, 106.59, 95.91, 87.51, 78.54, 30.01, 21.33, 17.43.

Ru–H ($[Ru(p\text{-}Cym)(dhpb\text{-}2H)H]^{-}$): ^{1}H NMR (300 MHz, $NaOD/D_2O$ 0.001 M) δ 7.38 (dd, *J* = 7.6, 8.0 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.30 (d, *J* = 7.5 Hz, 2H), 5.48 (d, *J* = 6.1 Hz, 2H), 5.12 (d, *J* = 6.0 Hz, 2H), 2.46 (s, 3H), 2.36 (hept, *J* = 6.9 Hz, 1H), 0.81 (d, *J* = 7.0 Hz, 6H), -6.55 (s, 1H). ^{13}C NMR (75 MHz, $NaOD/D_2O$ 0.001 M) δ 173.18, 156.19, 137.20, 112.95, 107.33, 101.98, 87.51, 78.54, 30.70, 22.15, 17.43.

Ru–H ($[Ru(p\text{-}Cym)(dhpb\text{-}2H)H]^{-}$): ^{1}H NMR (300 MHz, CD_3OD) δ 7.31 (t, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 7.1 Hz, 2H), 6.47 (d, *J* = 8.5 Hz, 2H), 5.66 (d, *J* = 5.2 Hz, 2H), 5.24 (d, *J* = 5.2 Hz, 2H), 2.56 (hept, *J* = 6.9 Hz, 1H), 2.49 (s, 3H), 1.03 (d, *J* = 6.6 Hz, 6H), -6.0 (s, 1H).

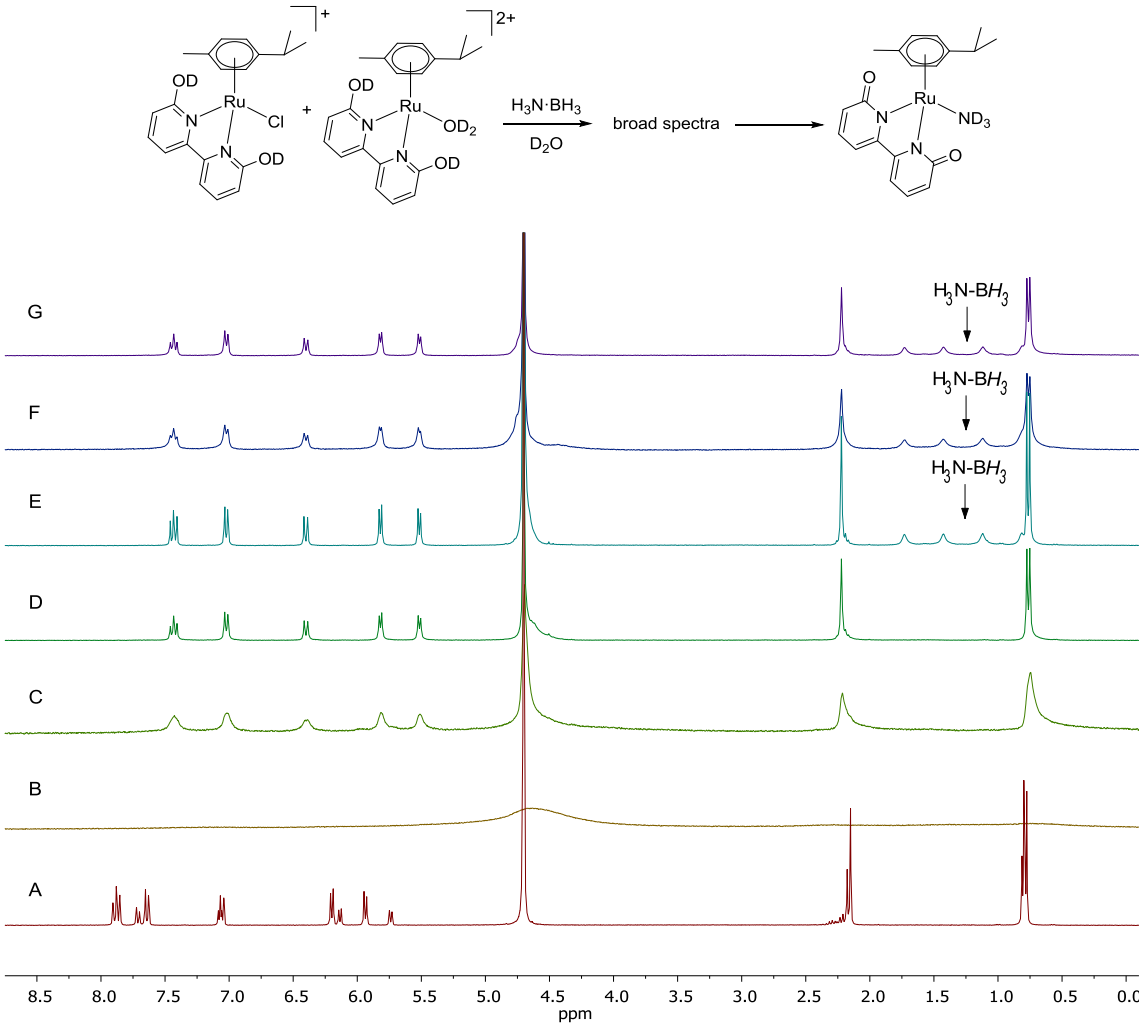


Figure S75. *In situ* ^{1}H NMR experiment (300 MHz, D_2O). **A** 0.75 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O. **B** Immediately after addition of 10 eq. of AB. **C** 13 minutes after addition of 10 eq. of AB. **D** 33 minutes after addition of 10 eq. of AB. **E** Immediately after second addition of 10 eq. of AB. **F** 19 minutes after second addition of 10 eq. of AB. **F** 35 minutes after second addition of 10 eq. of AB.

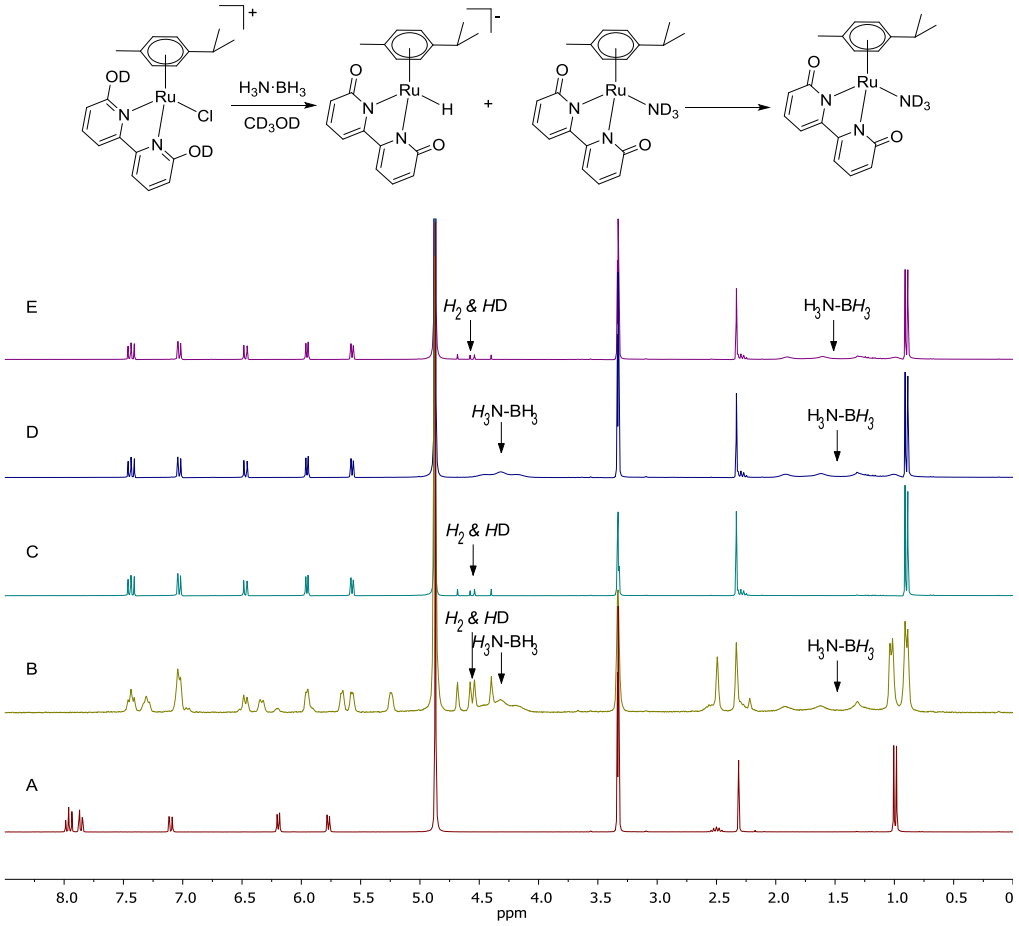


Figure S76. *In situ* ^{1}H NMR experiment (300 MHz, CD_3OD). **A** 0.75 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD. **B** Immediately after addition of 10 eq. of AB. **C** 18 minutes after addition of 10 eq. of AB. **D** Immediately after second addition of 10 eq. of AB. **E** 30 minutes after second addition of 10 eq. of AB. Hydride region not shown (see Figure S31).

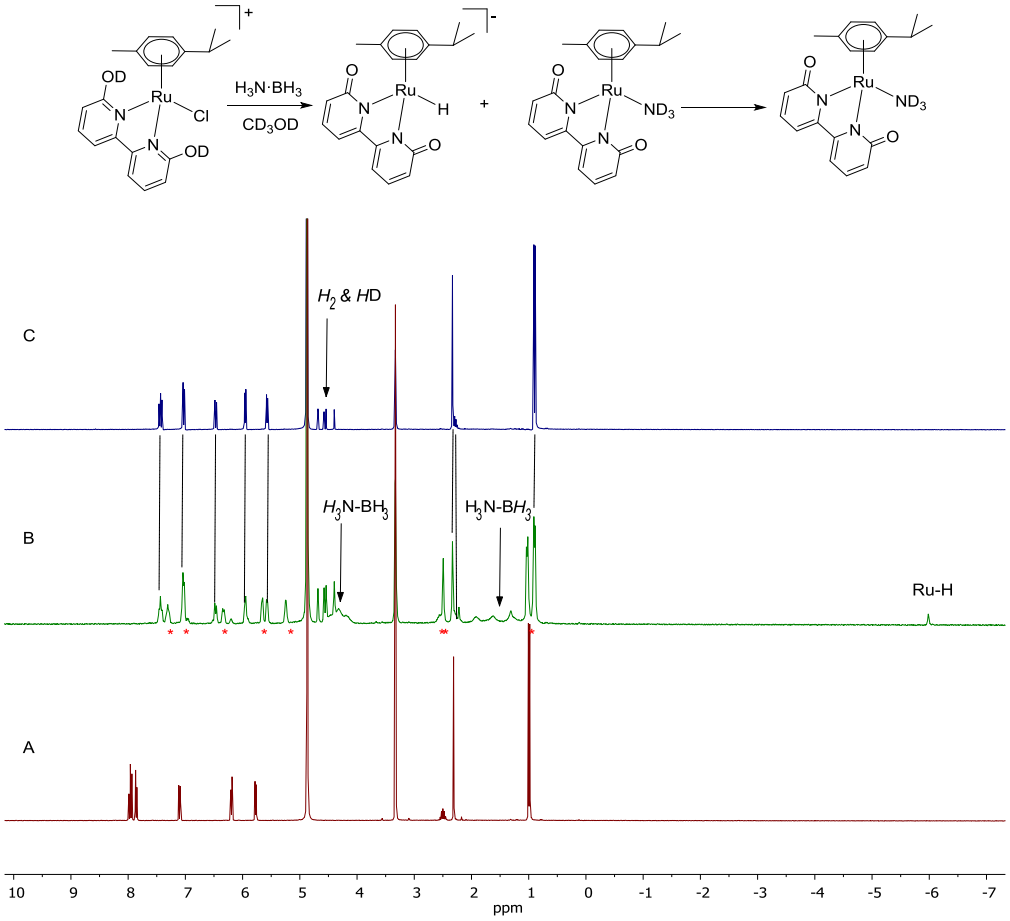
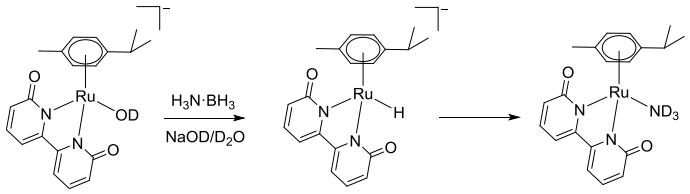
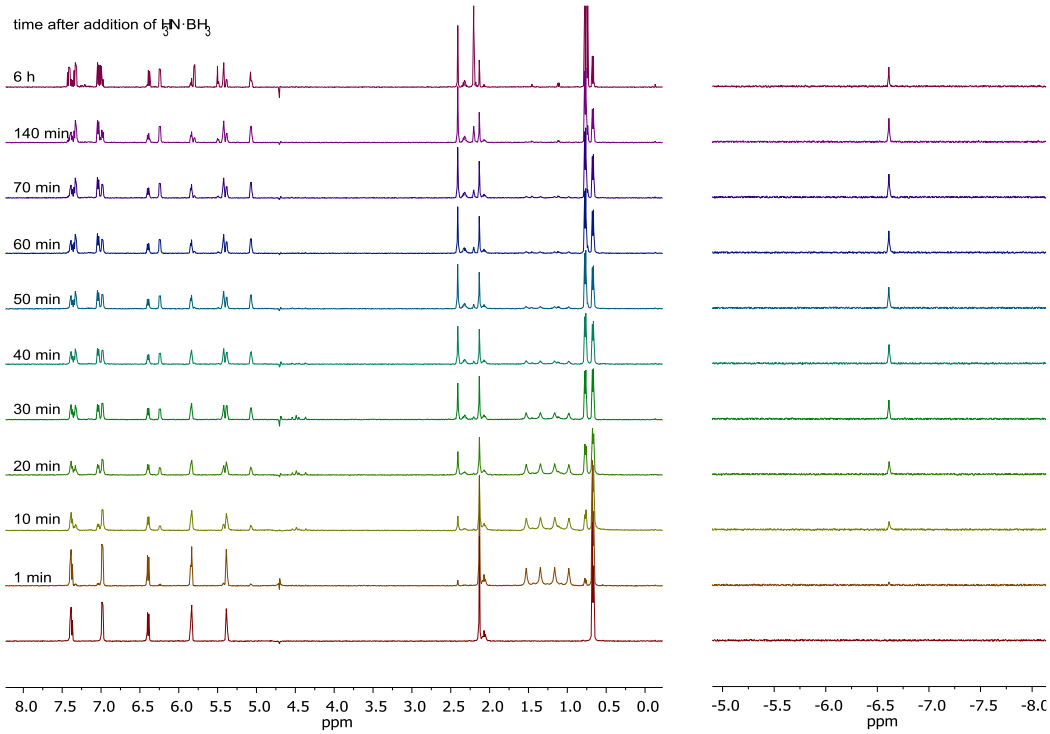


Figure S77. *In situ* ^{1}H NMR experiment (300 MHz, CD_3OD). **A** 0.75 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD. **B** Immediately after addition of 10 eq. of AB. **C** 3 minutes after addition of 10 eq. of AB. Signals marked with * are attributed to an *in situ* generated ruthenium-hydride.



^{1}H NMR



^{11}B NMR

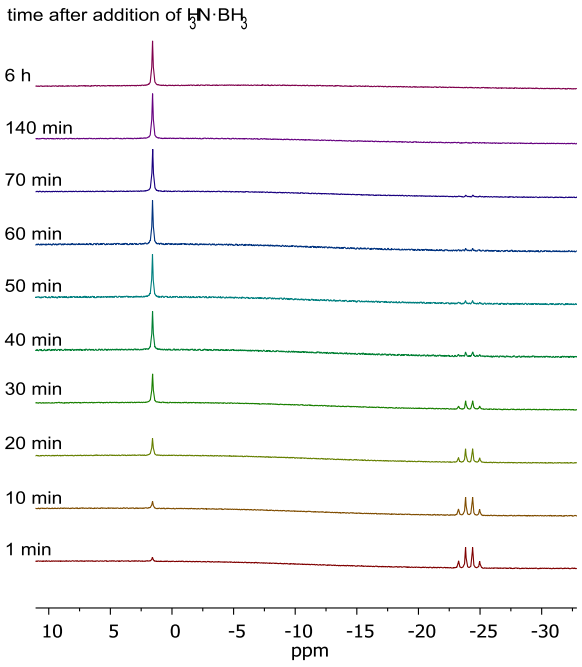


Figure S78. *In situ* NMR experiment. 0.75 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of NaOD/D_2O 0.001 M. Sequential spectra after addition of 10 eq. of AB. TOP: ^{1}H NMR, water signal suppression (500 MHz) BOTTOM: ^{11}B NMR (160 MHz)

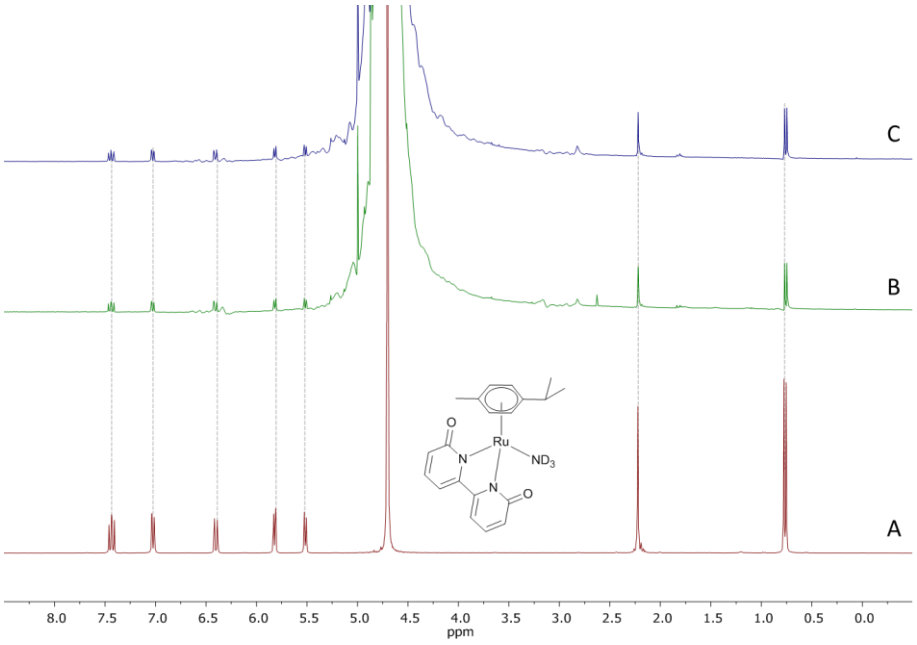


Figure S79. ^{1}H NMR spectra (300 MHz). **A.** 3.89 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of D_2O + 20 µL NH_3 aq. 20% v/v. **B.** Reaction solution at the end of a catalytic run using [Ru(p-Cym)(dhbp)Cl]Cl (**1**) as catalyst in H_2O (internal capillary of D_2O). **C.** Reaction solution at the end of a catalytic run using [Ru(p-Cym)(dhbp)(H_2O)](OTf)$_2$ (**2**) as catalyst in H_2O (internal capillary of D_2O).

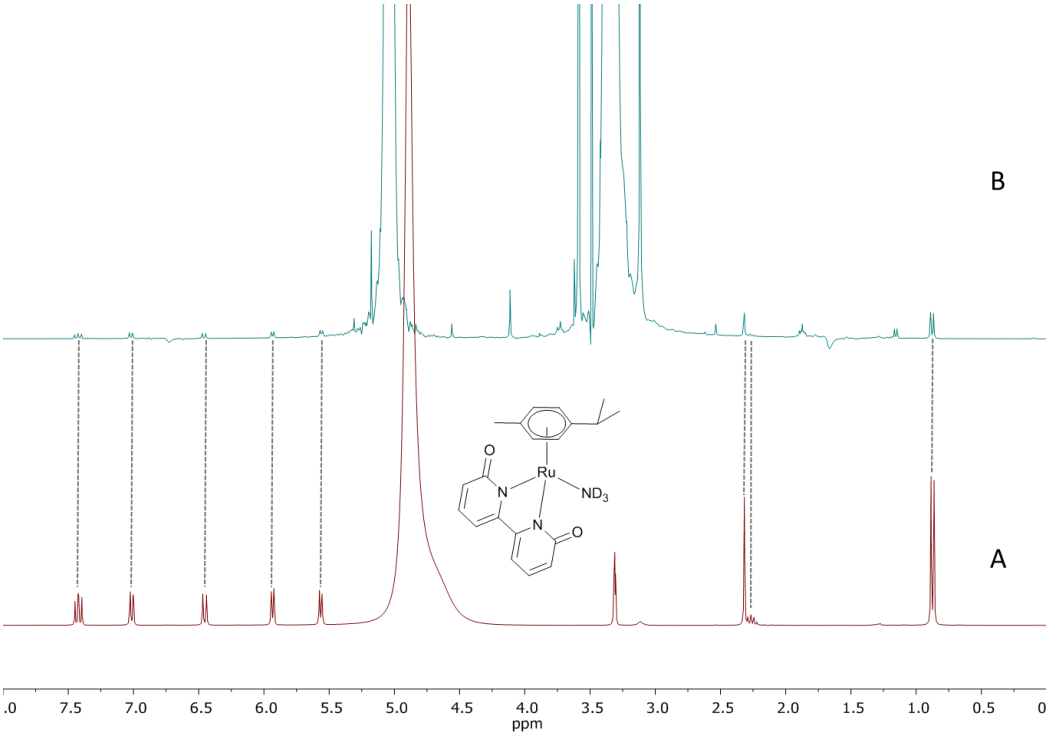


Figure S80. ^{1}H NMR spectra (300 MHz). **A** 3.85 mg of [Ru(p-Cym)(dhbp)Cl]Cl (**1**) in 0.5 mL of CD_3OD + 20 µL NH_3 aq. 20% v/v. **B** Reaction solution at the end of a catalytic run using [Ru(p-Cym)(dhbp)Cl]Cl (**1**) as catalyst in CH_3OH (internal capillary of D_2O).

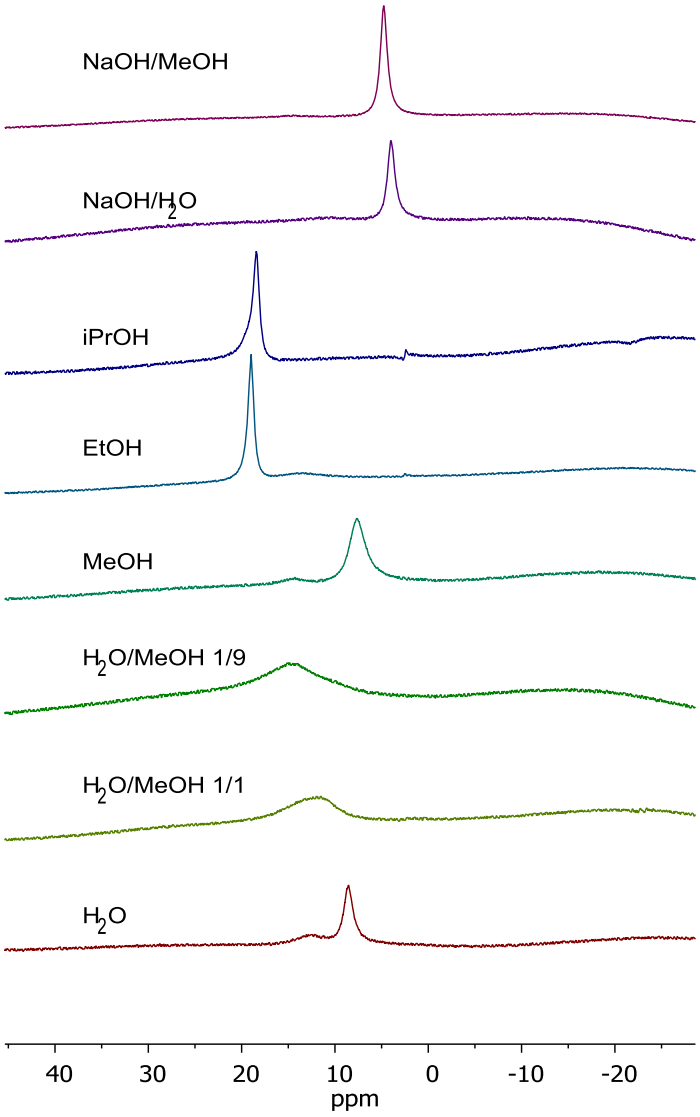
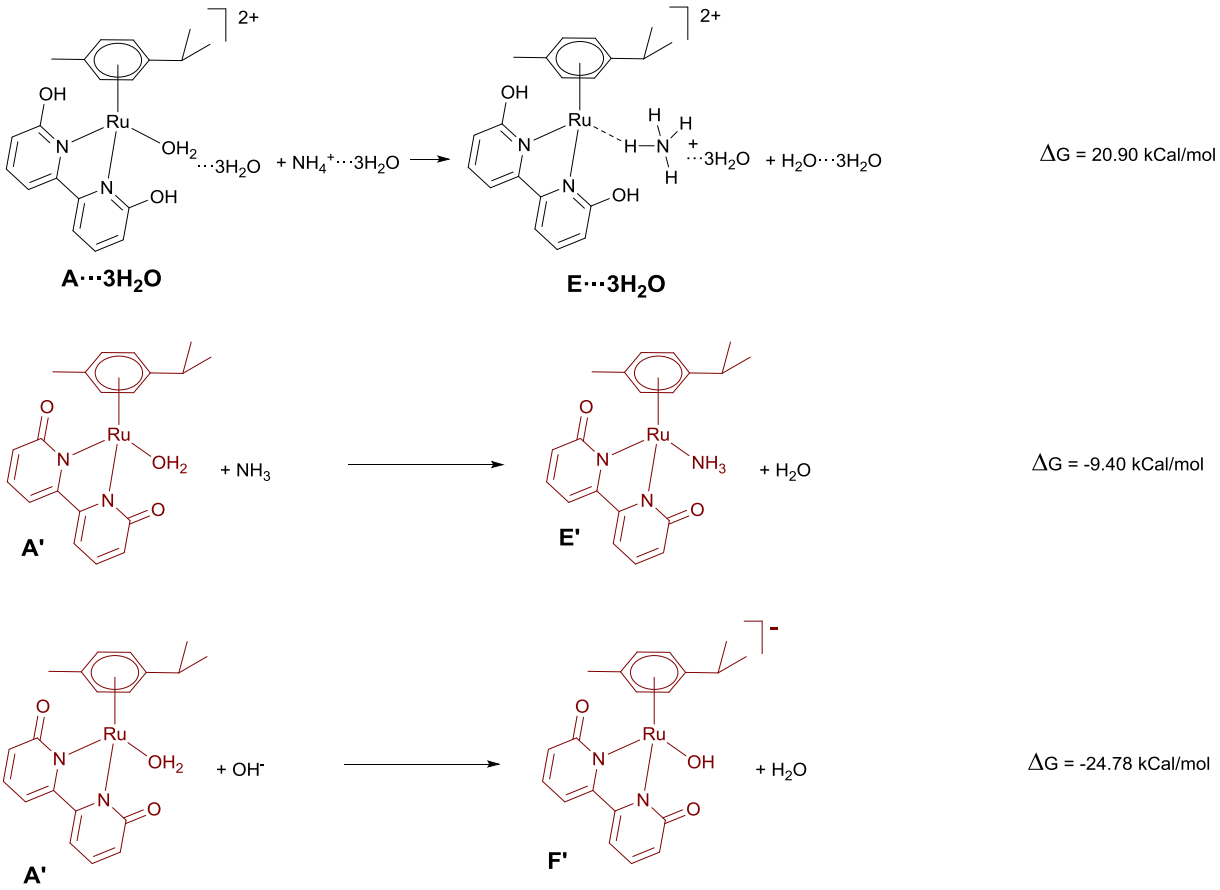
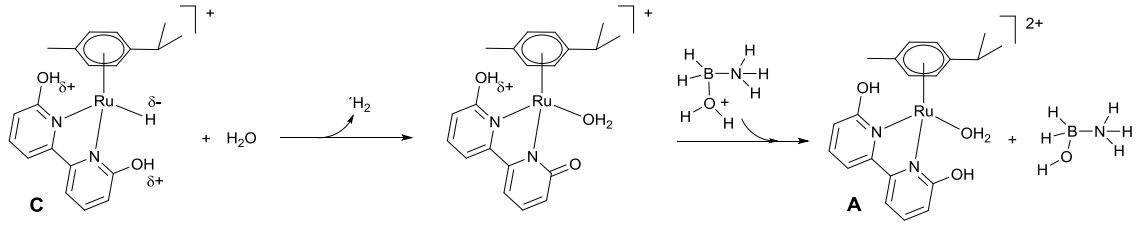


Figure S81. ^{11}B NMR spectra (128 MHz) of reaction solutions at the end of a catalytic run using [Ru(p-Cym)(dhbp)Cl]Cl (**1**) as catalyst in different solvents. ^{11} B NMR spectra at the end of the catalytic reactions show broad bands in the region 2–19 ppm which are characteristic of H_3BO_3, BO_2^- and other borate species in equilibrium in solution, and dependent on the pH of the reaction media, as described before by other authors.[1-2]

Mechanistic considerations and DFT calculations.



Scheme S3. Ligands exchange processes and estimated ΔG, according to DFT calculations.



Scheme S4. Alternative reaction pathway for the hydrogen-generation step with dhbp-protonated system.

Table S3. Summary of the energetic values (Hartree) of the calculated species.

species	Hsol	Gsol
OH^-	-75.907618	-75.927174
NH_3	-56.516436	-56.539314
Ru–OH: F' in Figure 6	-1204.204479	-1204.282803
Ru–NH_3: E' in Figure 6	-1184.791535	-1184.870430
Ru–H_2: D' in Figure 6	-1129.396869	-1129.473677
Ru–H: C' in Figure 6	-1128.960399	-1129.036651
Ru–BH_3NH_3: B' in Figure 6	-1211.404513	-1211.486632
Ru–H_2O: A' in Figure 6	-1204.665720	-1204.744231
H_2O···3 H_2O	-305.641754	-305.693080
NH_4^+···3 H_2O	-286.190072	-286.242854
H_2	-1.156178	-1.170957
HO-BH_2NH_3	-158.406529	-158.438838
H_2O-$BH_2NH_3^+$	-158.819703	-158.853927
H_2O	-76.406671	-76.428098
BH_3NH_3	-83.136674	-83.164781
Ru–H_2O···3 H_2O: A···3 H_2O in Figure 6	-1434.780776	-1434.877283
Ru–NH_4^+···3 H_2O: E···3 H_2O in Figure 6	-1415.295754	-1415.393755
Ru–H_2: D in Figure 6	-1130.248629	-1130.326511
Ru–H: C in Figure 6	-1129.853349	-1129.930263
Ru–BH_3NH_3: B in Figure 6	-1212.268613	-1212.352748
Ru–H_2O: A in Figure 6	-1205.531903	-1205.612979

Homogeneity tests.

The homogeneous nature of the catalyst was investigated by running selected catalytic reactions in presence of 1000 eq. of mercury per catalyst. The similar reaction profiles obtained with and without added mercury (within the experimental error) permitted us to confirm the homogeneity of the catalyst during the active catalytic period. The differences observed during the less active period, does not permit us to completely discard that nanoparticles were responsible of part of the activity observed at extended reaction times.

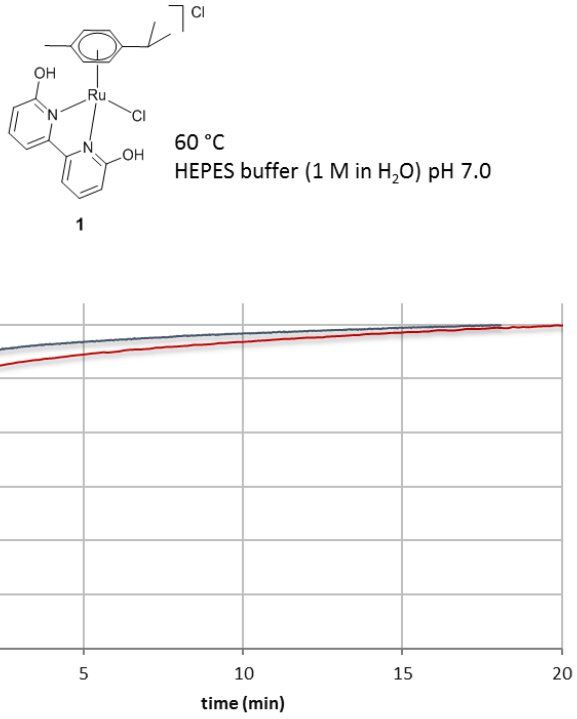


Figure S82. Reaction profiles of AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 4). Conditions: blue line: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL (HEPES buffer 1 M in H_2O, pH 7.0), 60 °C. red line: [Ru] = 2.3 mM, [AB] = 0.46 M, Hg (1000 equiv. per Ru), 1.5 mL (HEPES buffer 1 M in H_2O, pH 7.0), 60 °C.

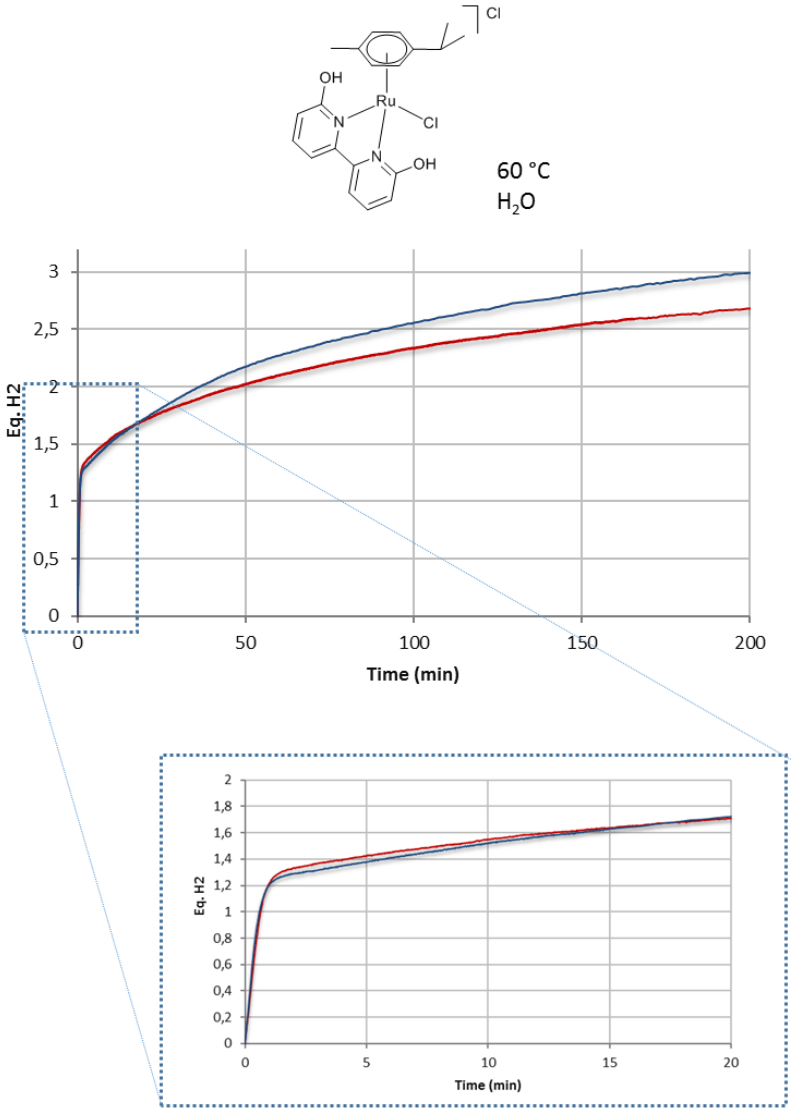


Figure S83. Reaction profiles of AB solvolysis using [Ru(p-Cym)(dhbp)Cl]Cl (**1**). (Table 2, Entry 4). Conditions: blue line: [Ru] = 2.3 mM, [AB] = 0.46 M, 1.5 mL H_2O, 60 °C. red line: [Ru] = 2.3 mM, [AB] = 0.46 M, Hg (1000 equiv. per Ru), 1.5 mL H_2O, 60 °C.

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