

## Preparation of Monocarbonyl Ruthenium Complexes Bearing Bidentate Nitrogen and Phosphine Ligands and their Catalytic Activity in the Carbonyl Compound Reduction.

Steven Giboulot,<sup>a,b</sup> Clara Comuzzi,<sup>a</sup> Alessandro Del Zotto,<sup>a</sup> Rosario Figliolia,<sup>a</sup> Giovanna Lippe,<sup>a</sup> Denise Lovison,<sup>a</sup> Paolo Strazzolini,<sup>a</sup> Sabina Susmel,<sup>a</sup> Ennio Zangrando,<sup>c</sup> Daniele Zuccaccia,<sup>a</sup> Salvatore Baldino,<sup>a,d</sup> Maurizio Ballico,<sup>a,\*</sup> Walter Baratta<sup>a,\*</sup>

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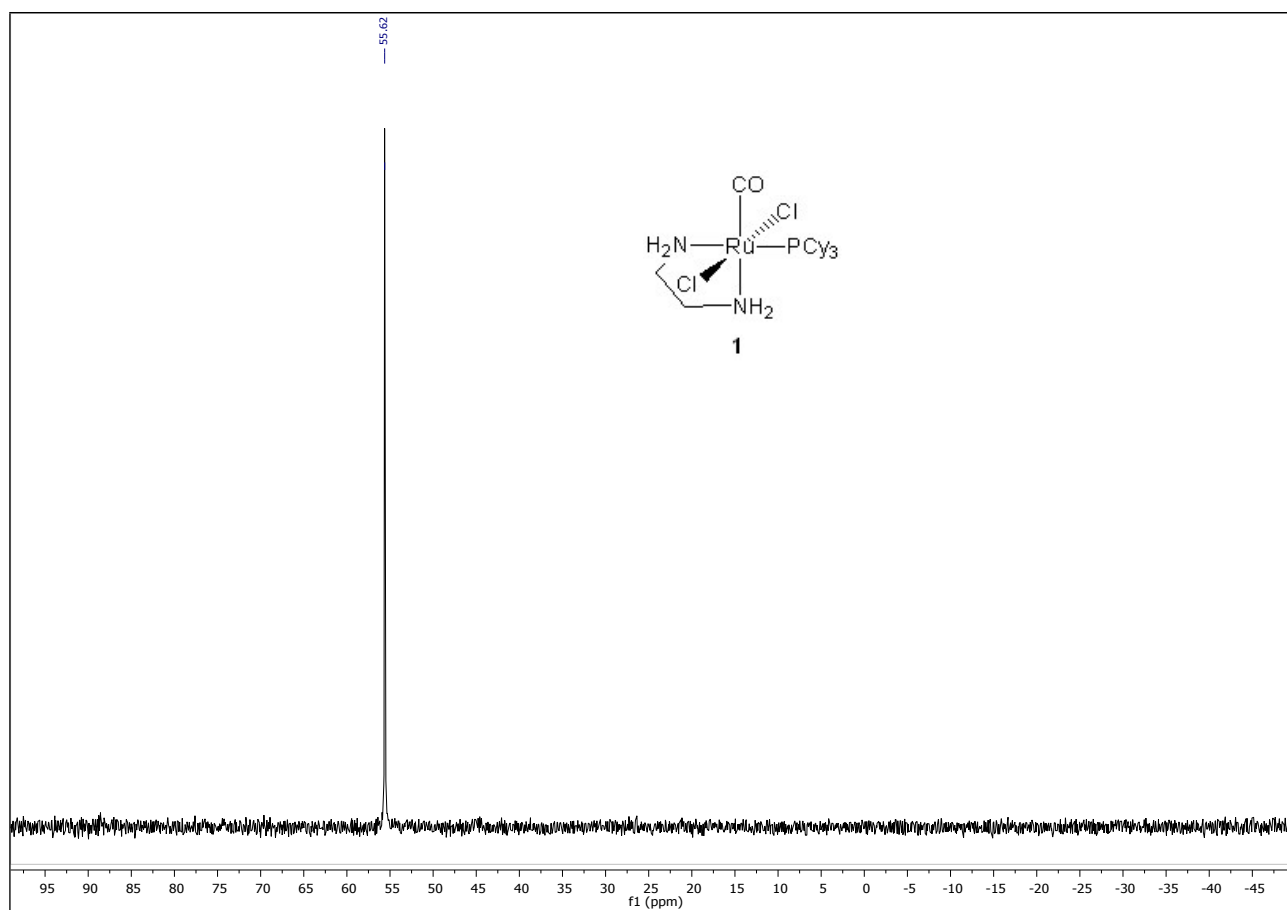
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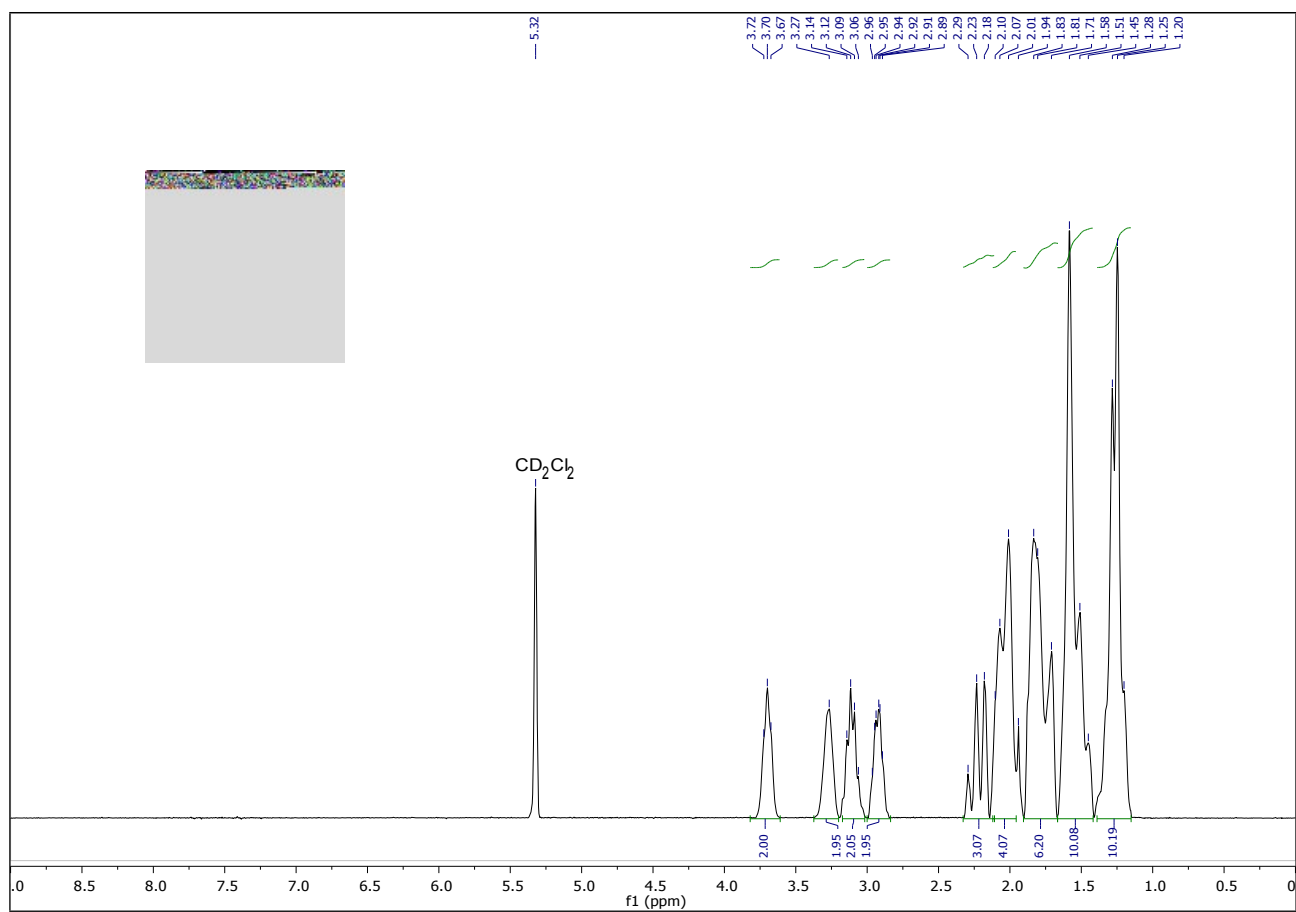
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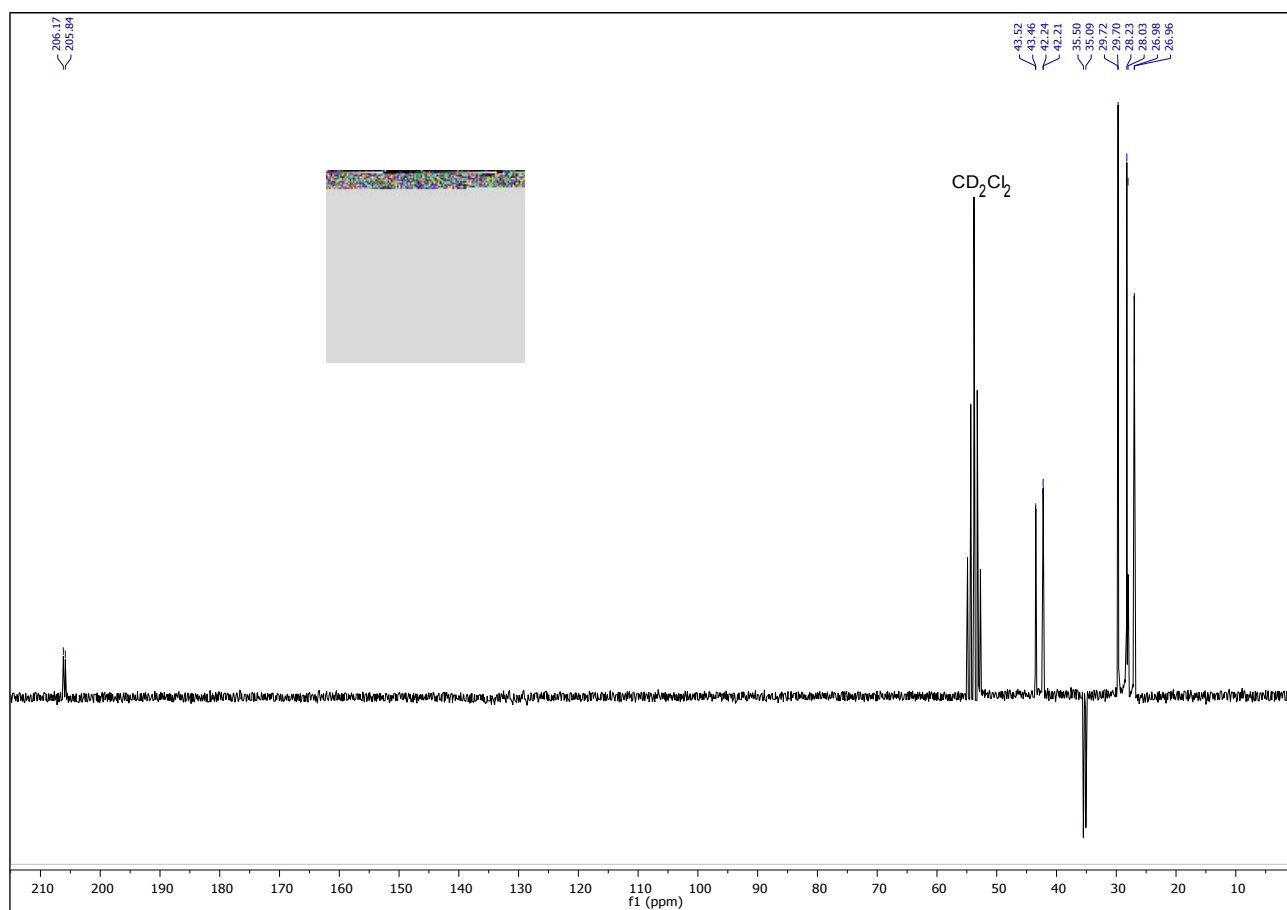
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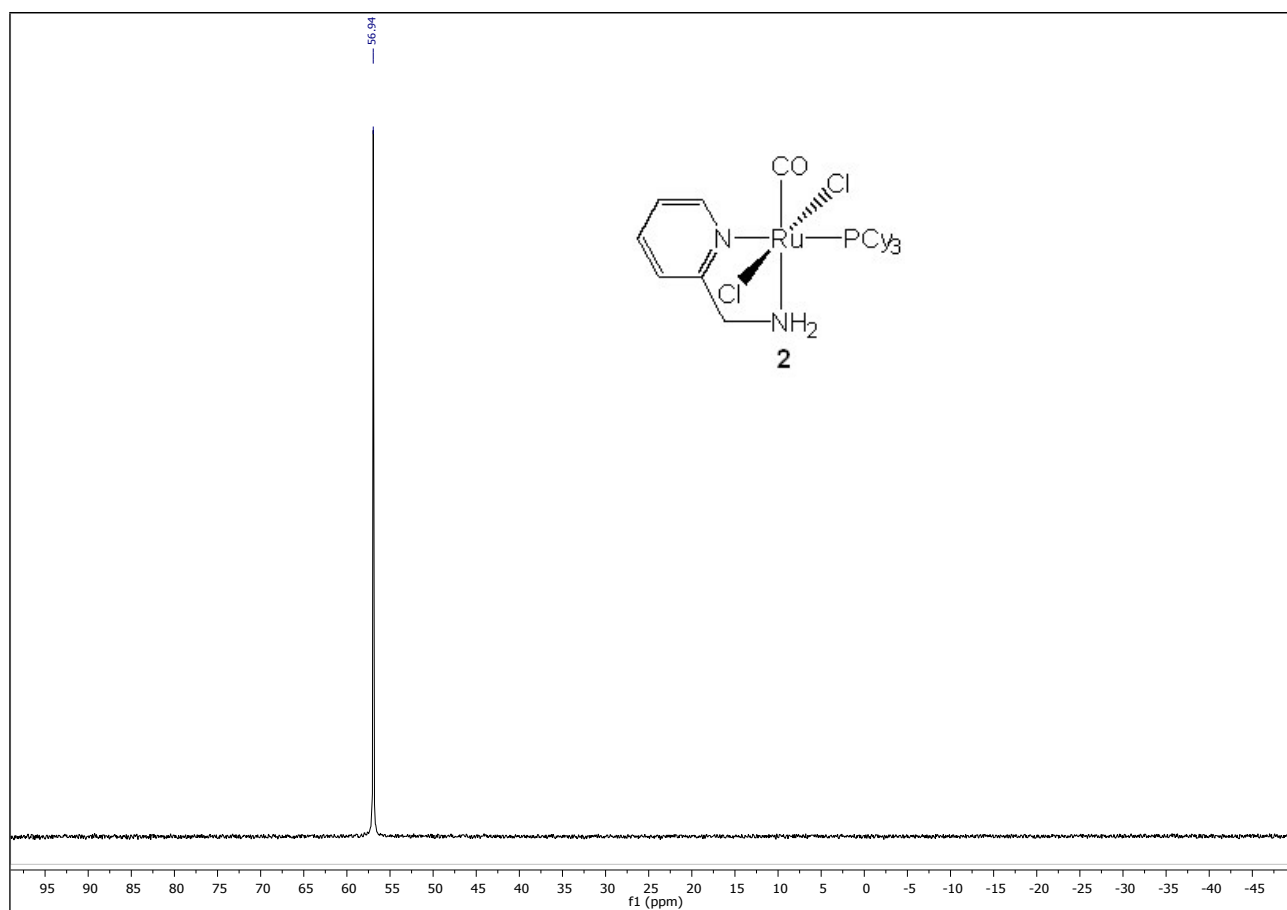


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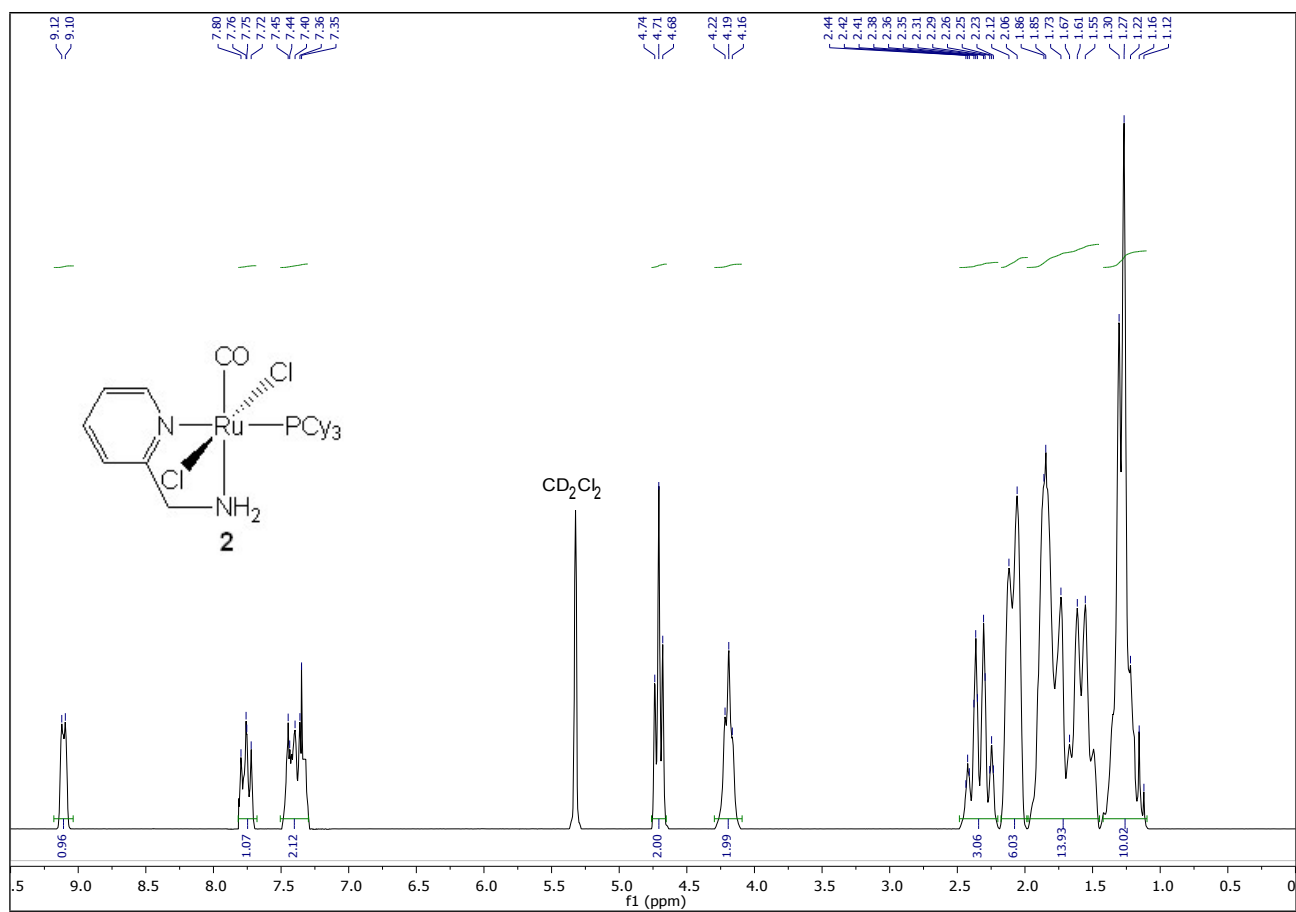


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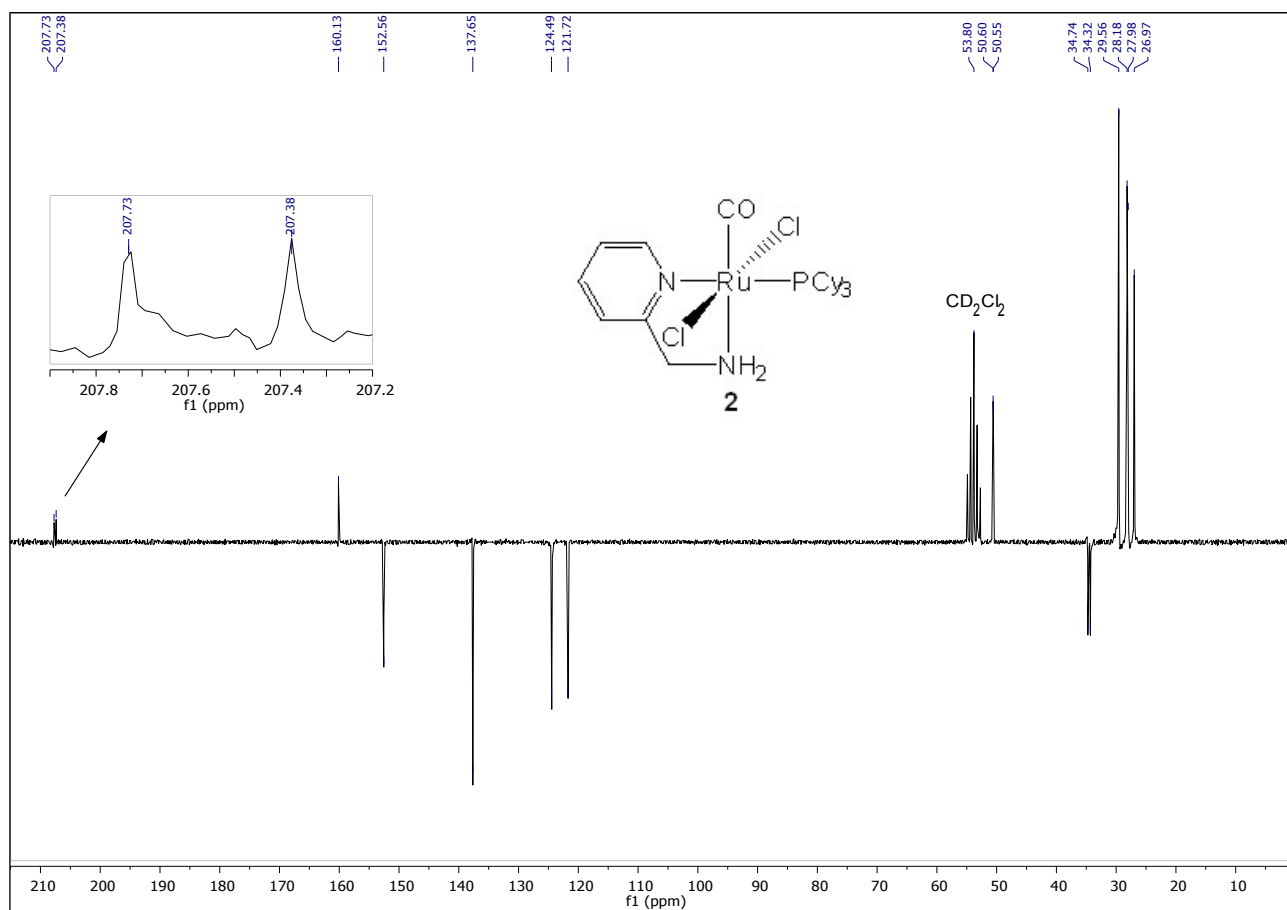




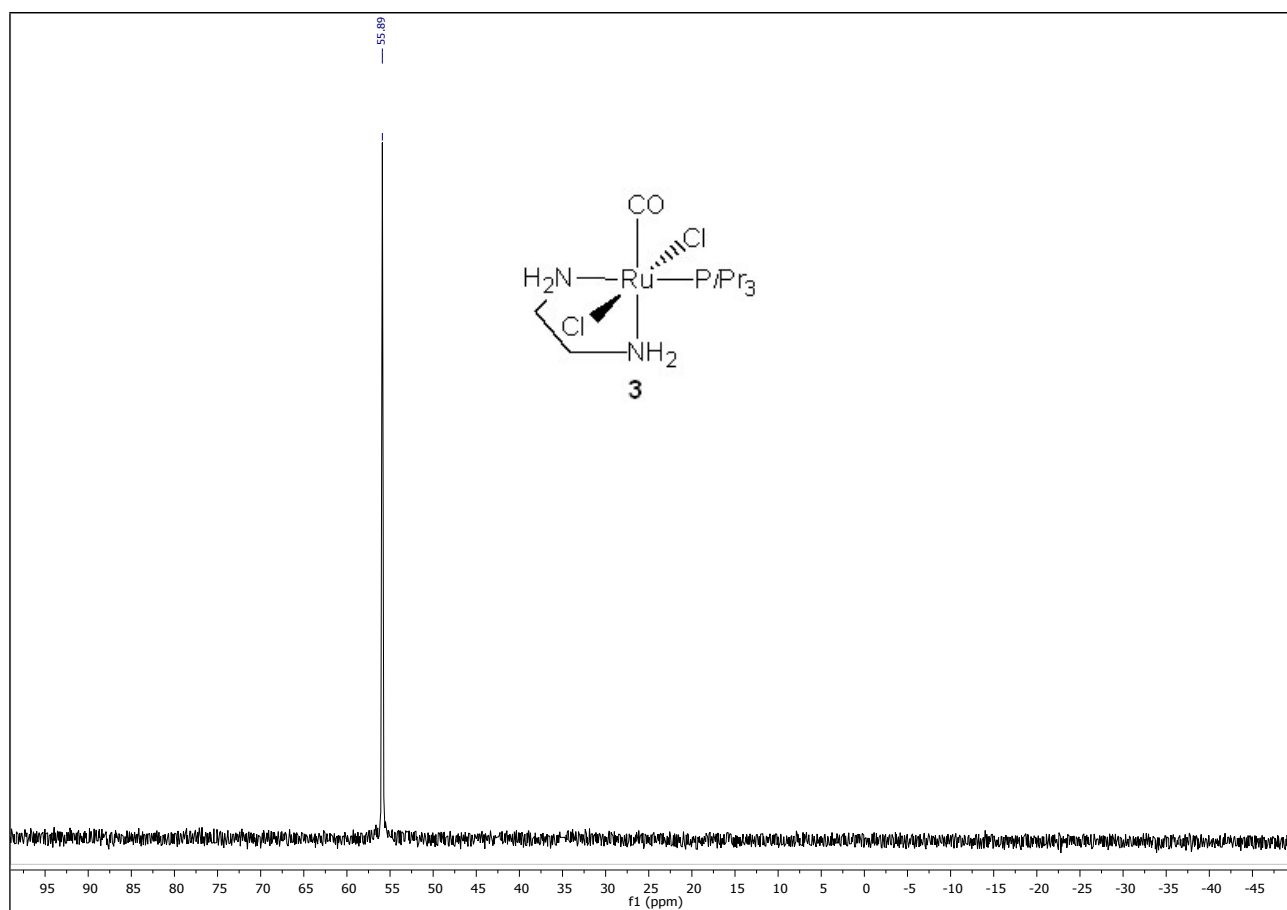
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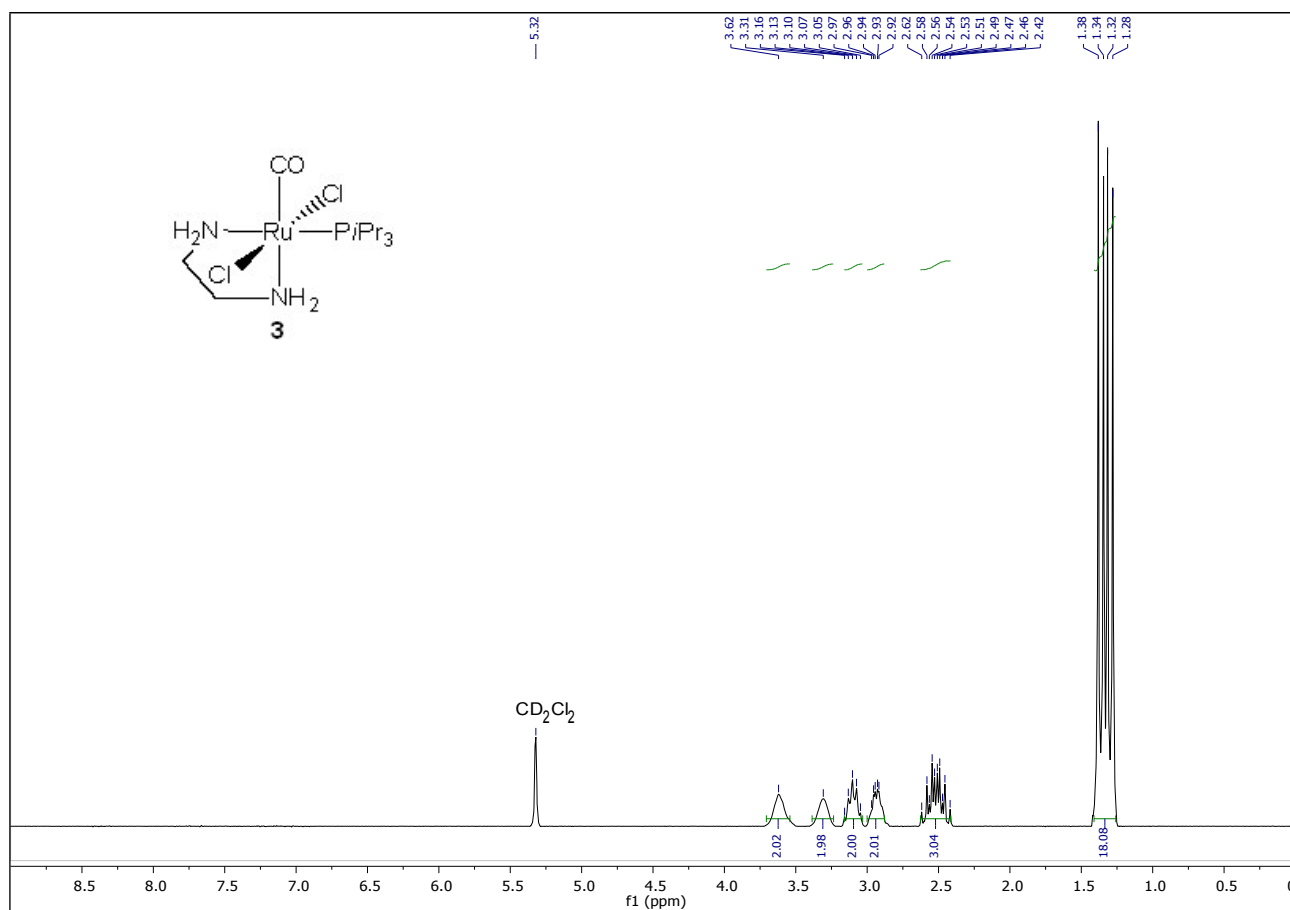
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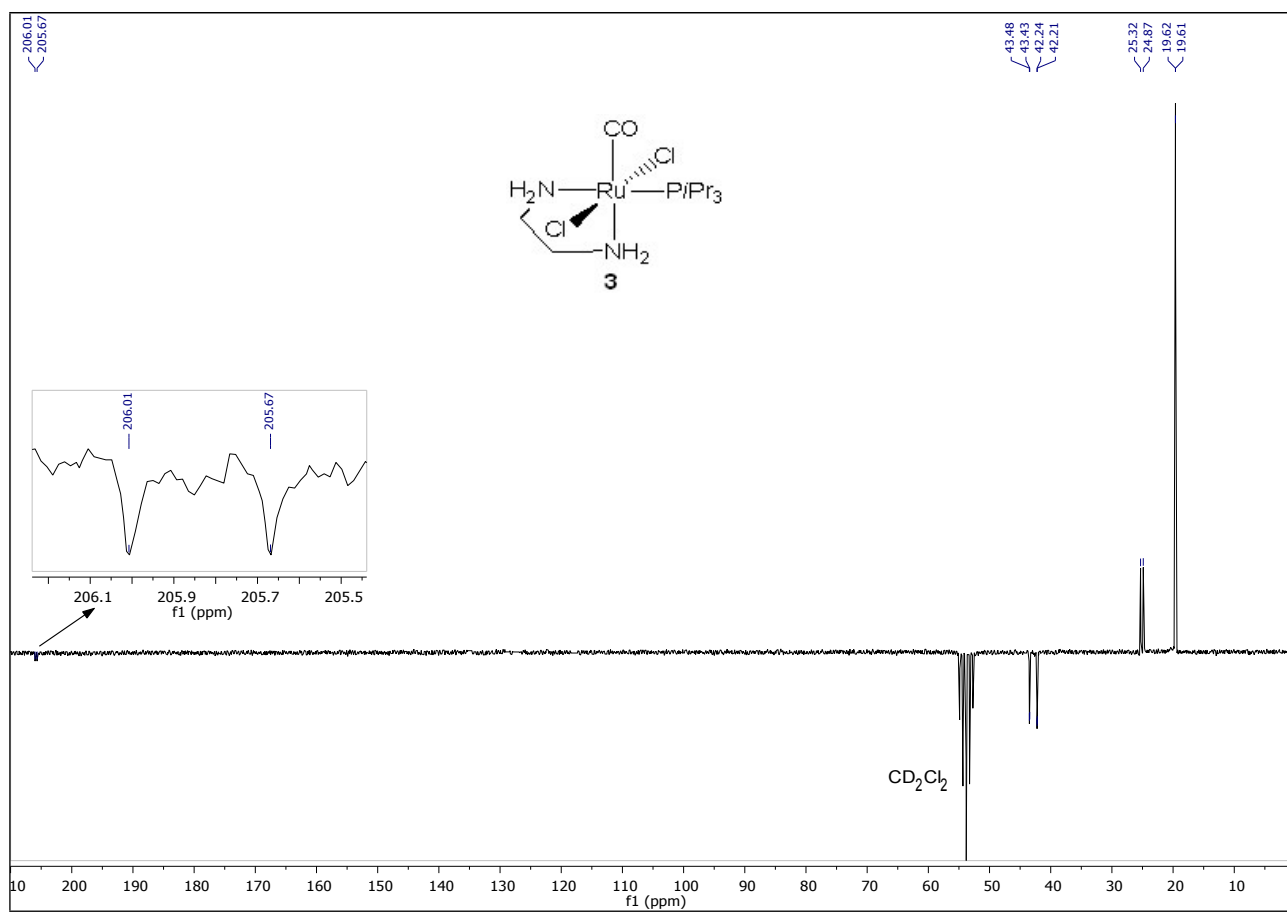
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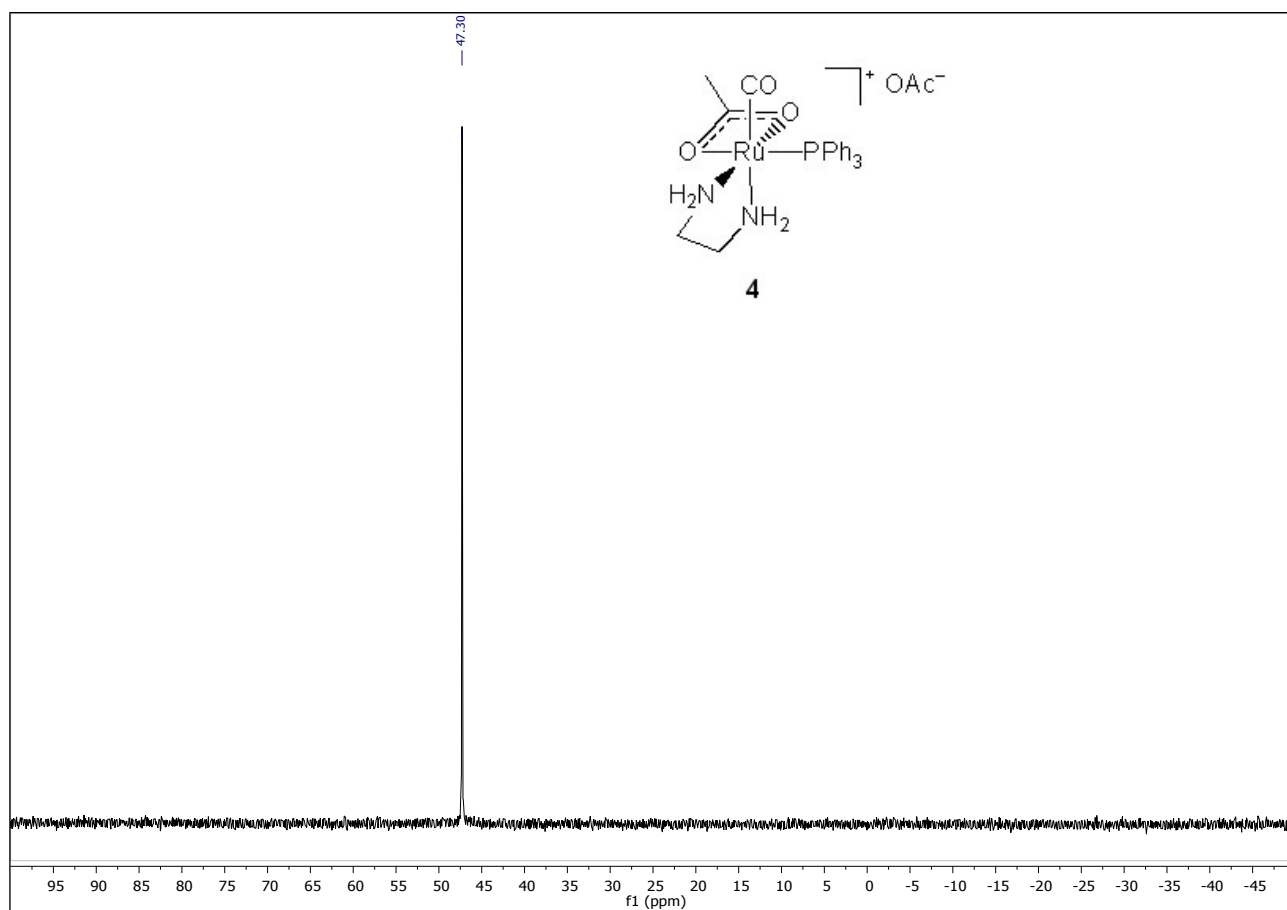
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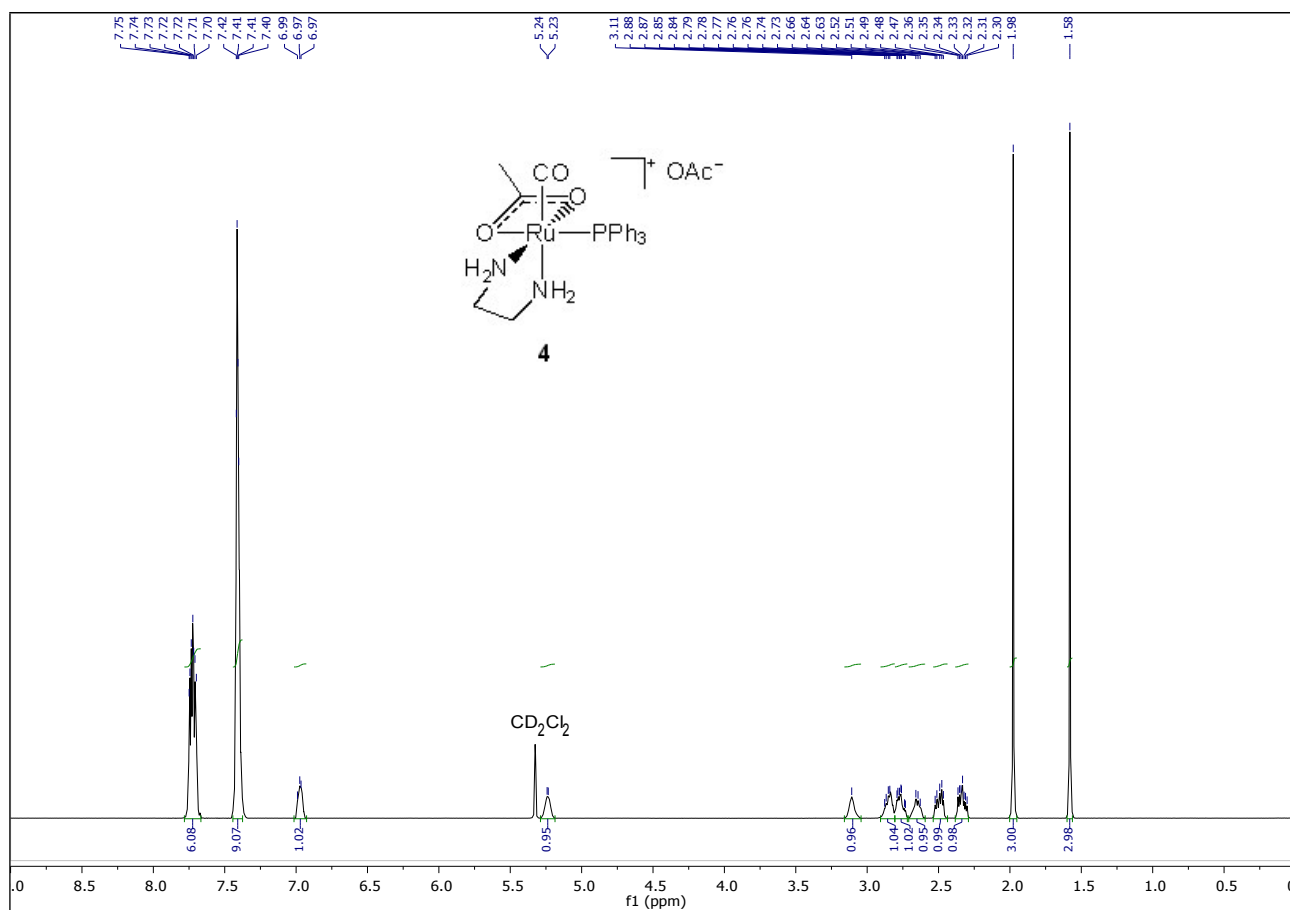
**Figure S8.**  $^1\text{H NMR}$  spectrum (200.1 MHz) of *trans*-[RuCl<sub>2</sub>(CO)(PiPr<sub>3</sub>)(en)] (**3**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.



**Figure S9.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $\text{trans-}[\text{RuCl}_2(\text{CO})(\text{PiPr}_3)(\text{en})]$  (**3**) in  $\text{CD}_2\text{Cl}_2$  at  $20\text{ }^\circ\text{C}$ .

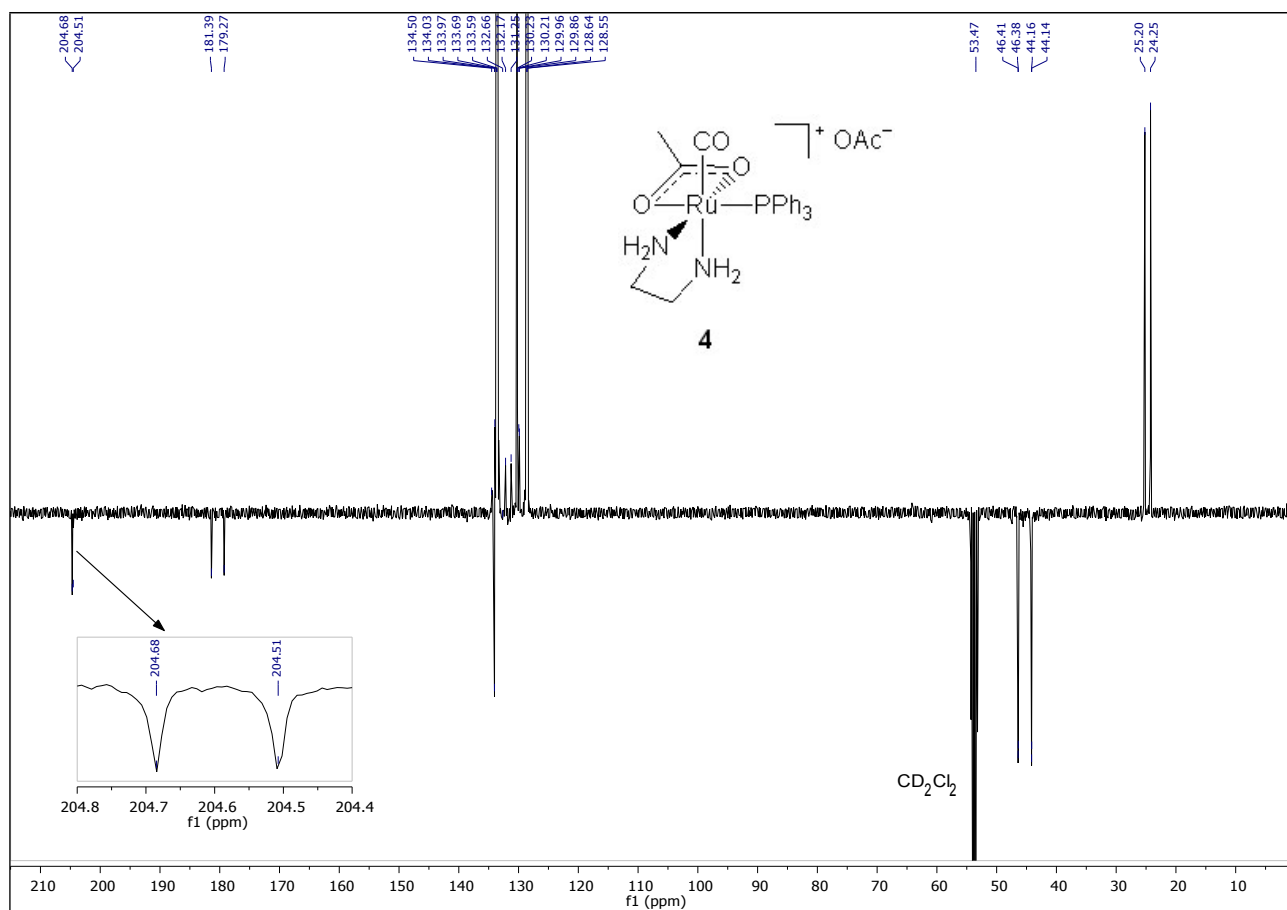


**Figure S10.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.0 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{PPh}_3)(\text{en})]\text{OAc}$  (**4**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.

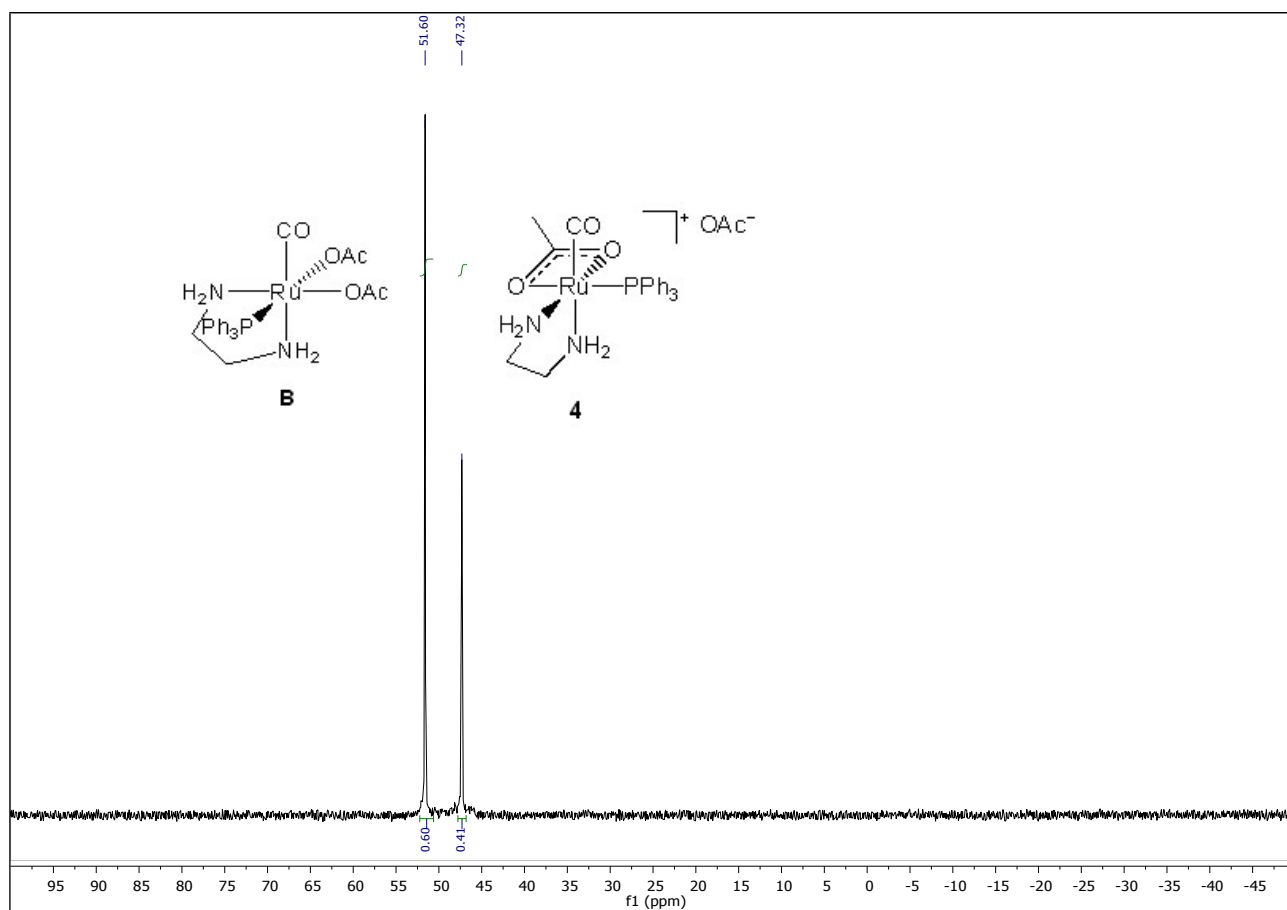


**Figure S11.** <sup>1</sup>H NMR spectrum (400.1 MHz) of [Ru(OAc)(CO)(PPh<sub>3</sub>)(en)]OAc (**4**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.

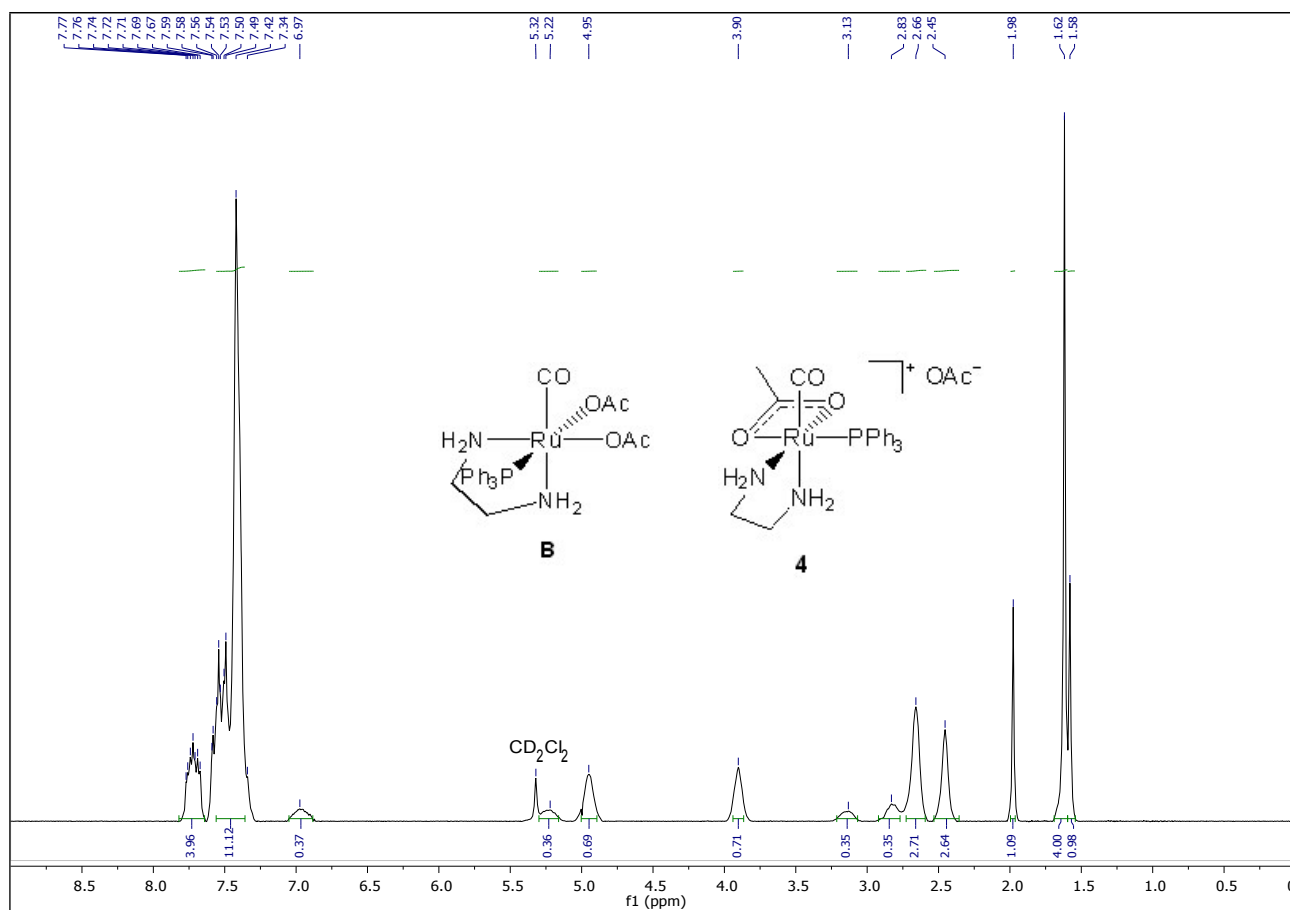




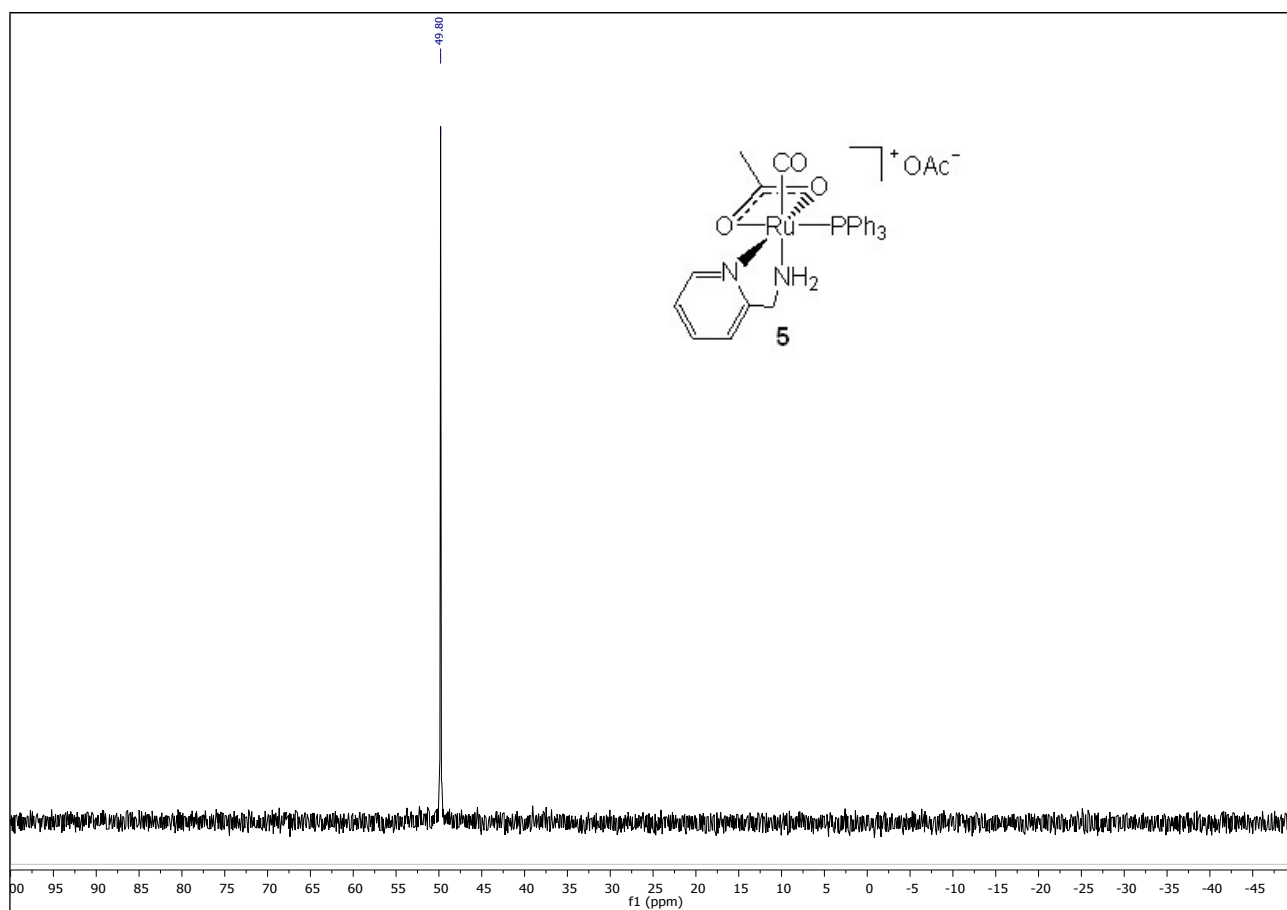
**Figure S12.** <sup>13</sup>C{<sup>1</sup>H} DEPTQ NMR spectrum (100.6 MHz) of [Ru(OAc)(CO)(PPh<sub>3</sub>)(en)]OAc (**4**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.



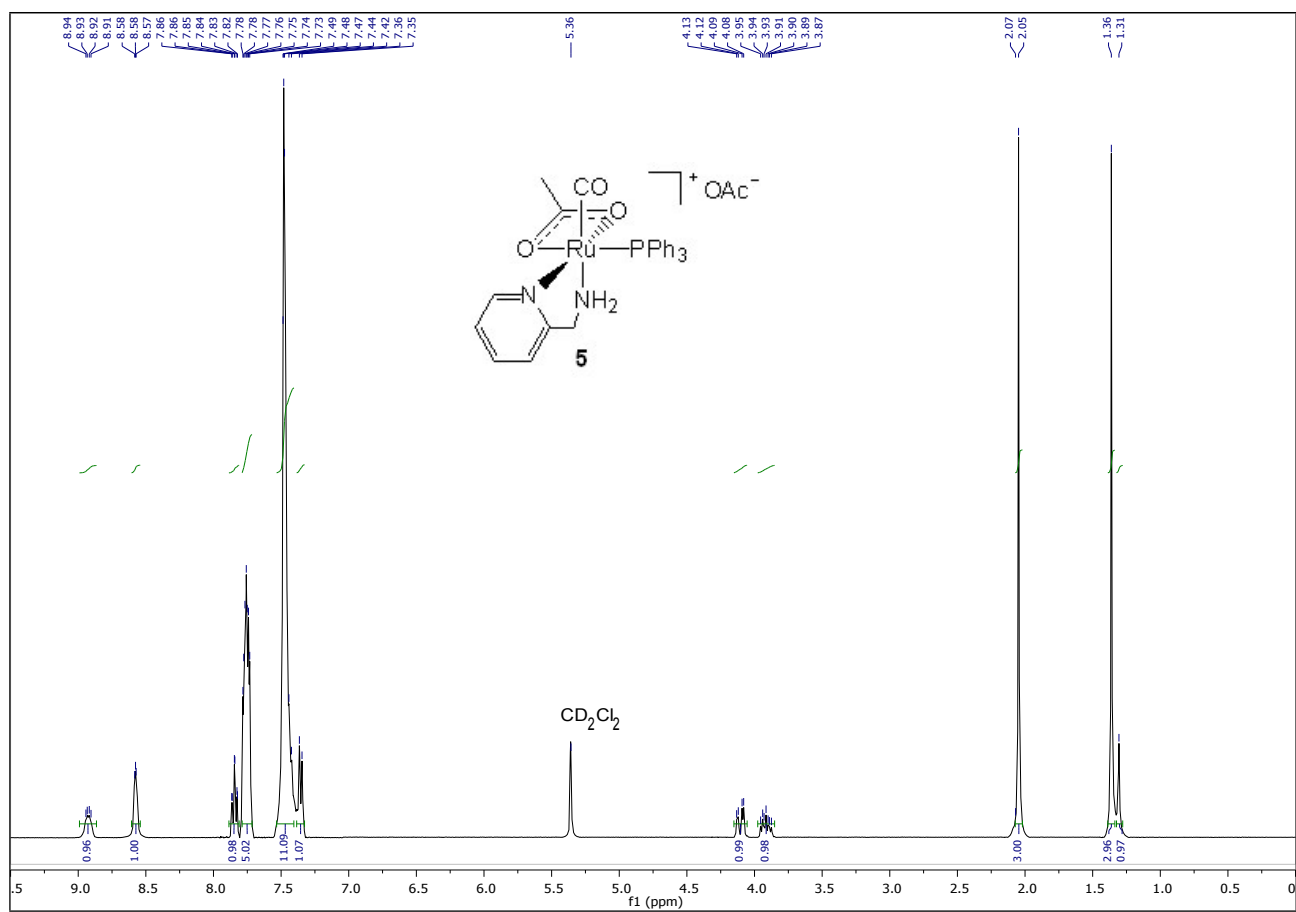
**Figure S13.** Control  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of the mixture of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{PPh}_3)(\text{en})]\text{OAc}$  (**4**) and  $\text{trans-}[\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)(\text{en})]$  (**B**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.



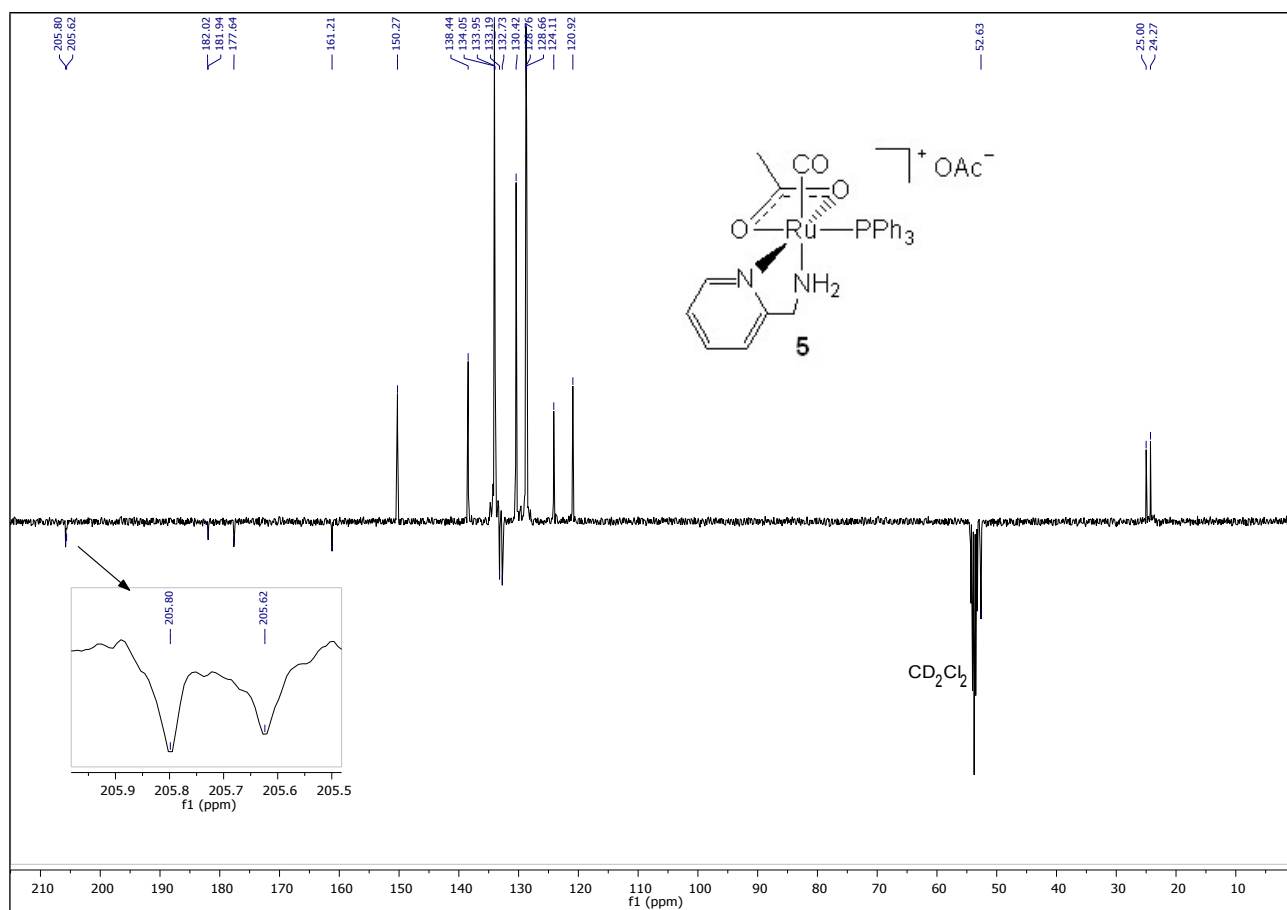
**Figure S14.** Control  $^1\text{H}$  NMR spectrum (200.1 MHz) of the mixture of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{PPh}_3)(\text{en})]\text{OAc}$  (**4**) and  $\text{trans-}[\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)(\text{en})]$  (**B**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.



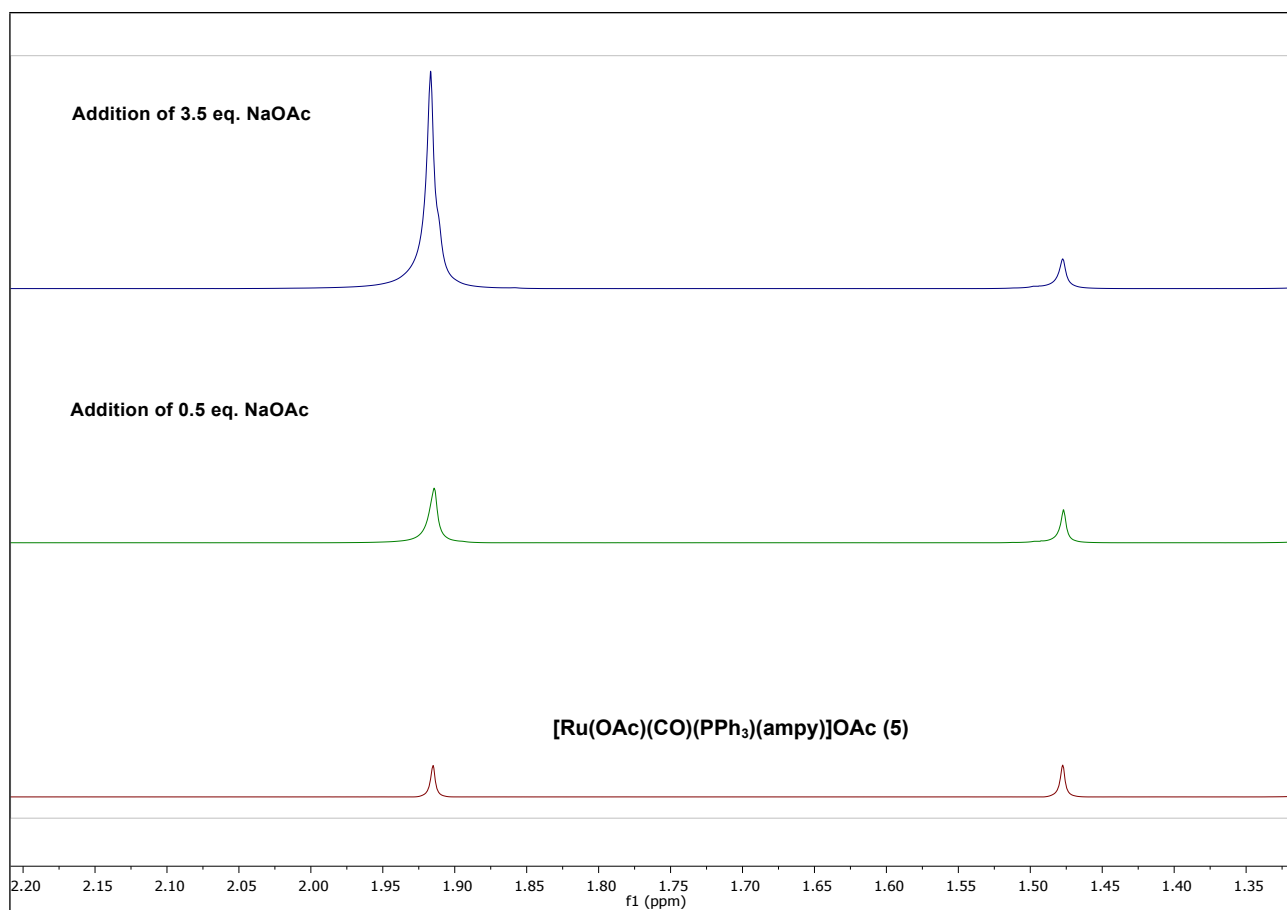
**Figure S15.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.0 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{PPh}_3)(\text{ampy})]\text{OAc}$  (**5**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.



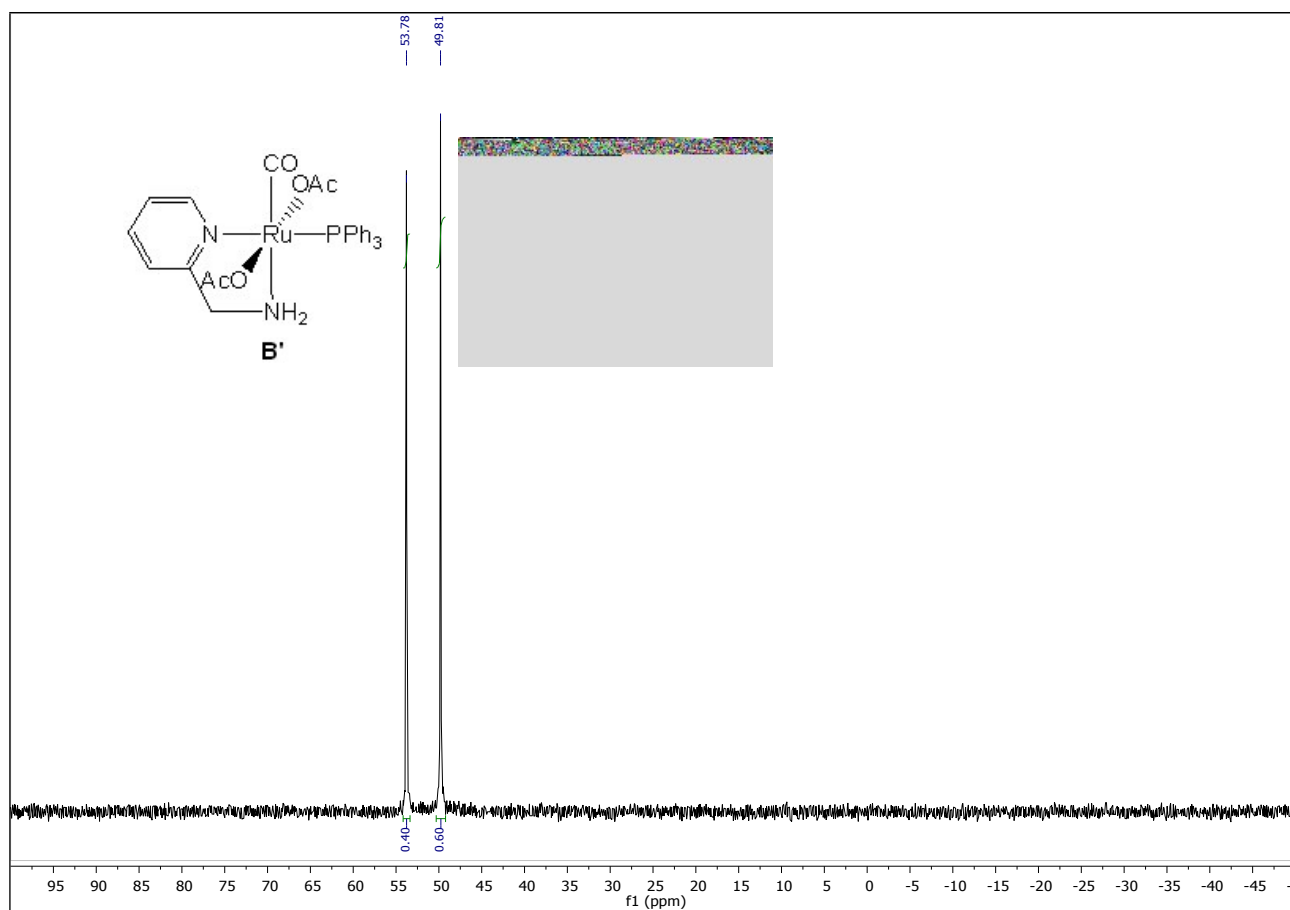
**Figure S16.** <sup>1</sup>H NMR spectrum (400.1 MHz) of [Ru(OAc)(CO)(PPh<sub>3</sub>)(ampy)]OAc (**5**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.



**Figure S17.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum (100.6 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{PPh}_3)(\text{ampy})]\text{OAc}$  (**5**) in  $\text{CD}_2\text{Cl}_2$  at  $20\text{ }^\circ\text{C}$ .

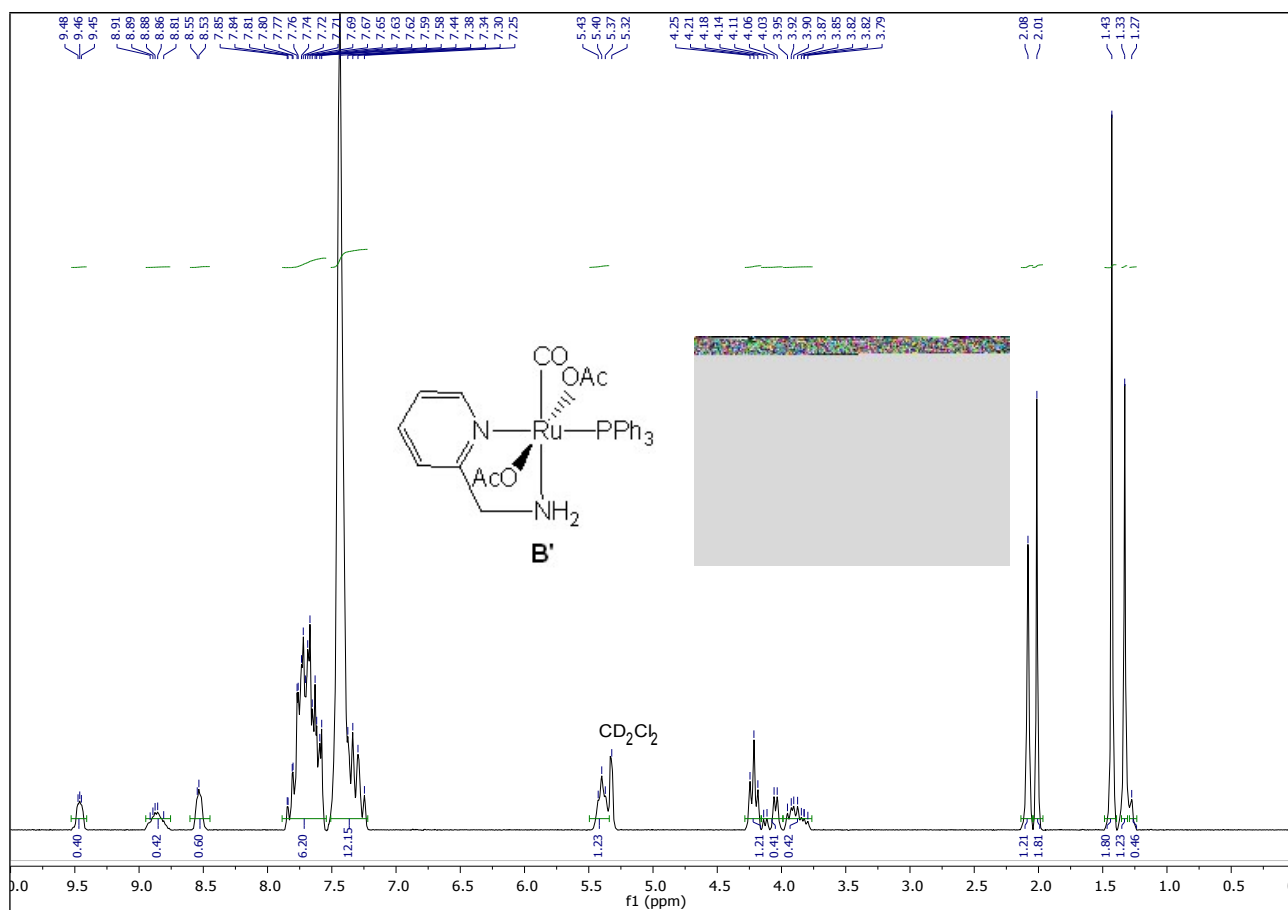


**Figure S18.** Effect of the addition of NaOAc to  $[\text{Ru}(\text{OAc})(\text{CO})(\text{PPh}_3)(\text{ampy})]\text{OAc}$  (**5**) in the methyl acetate region of the  $^1\text{H}$  NMR spectra in  $\text{CD}_3\text{OD}$  at 20 °C.

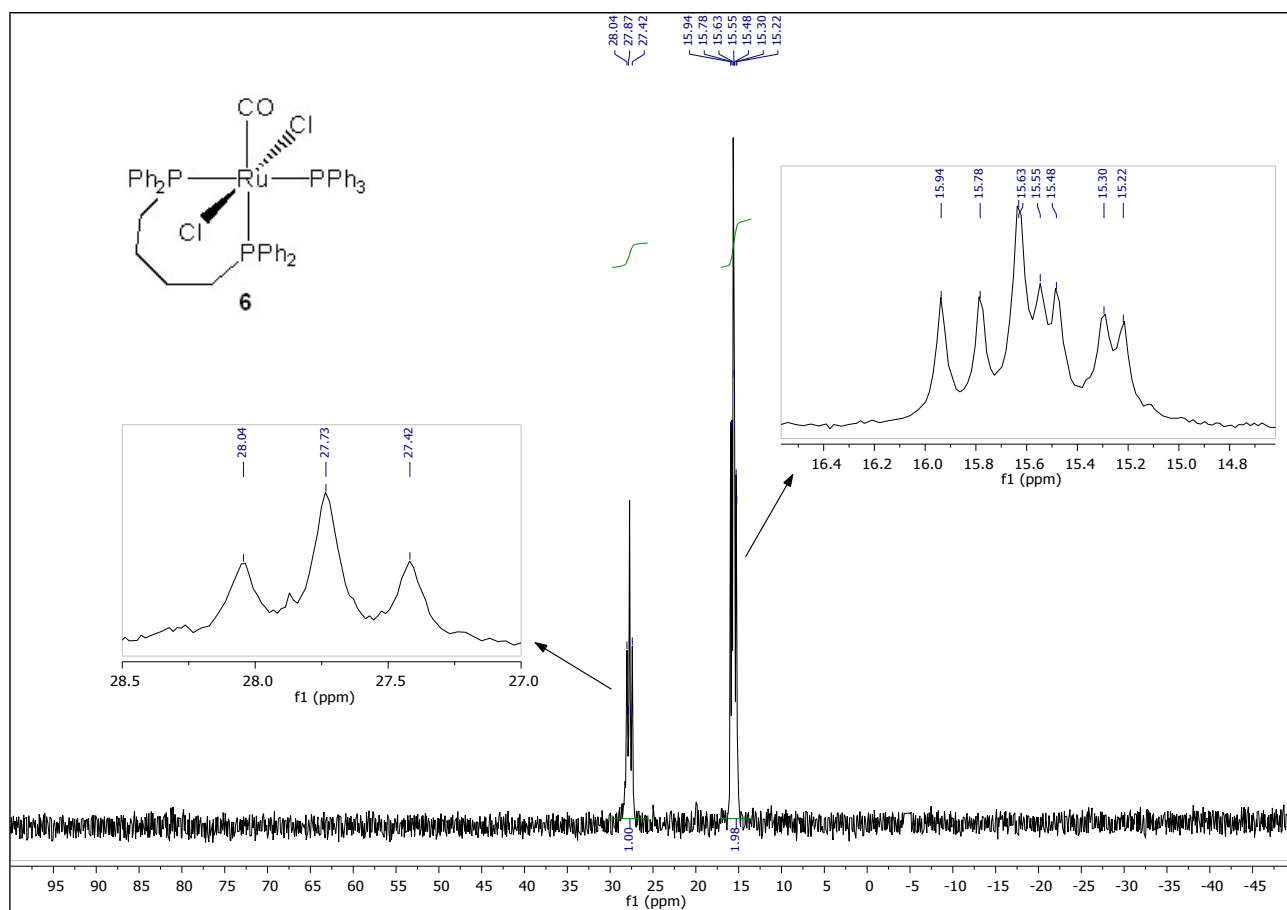


**Figure S19.** Control  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of the mixture of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{PPh}_3)(\text{ampy})]\text{OAc}$  (**5**) and *trans*- $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)(\text{ampy})]$  (**B'**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.

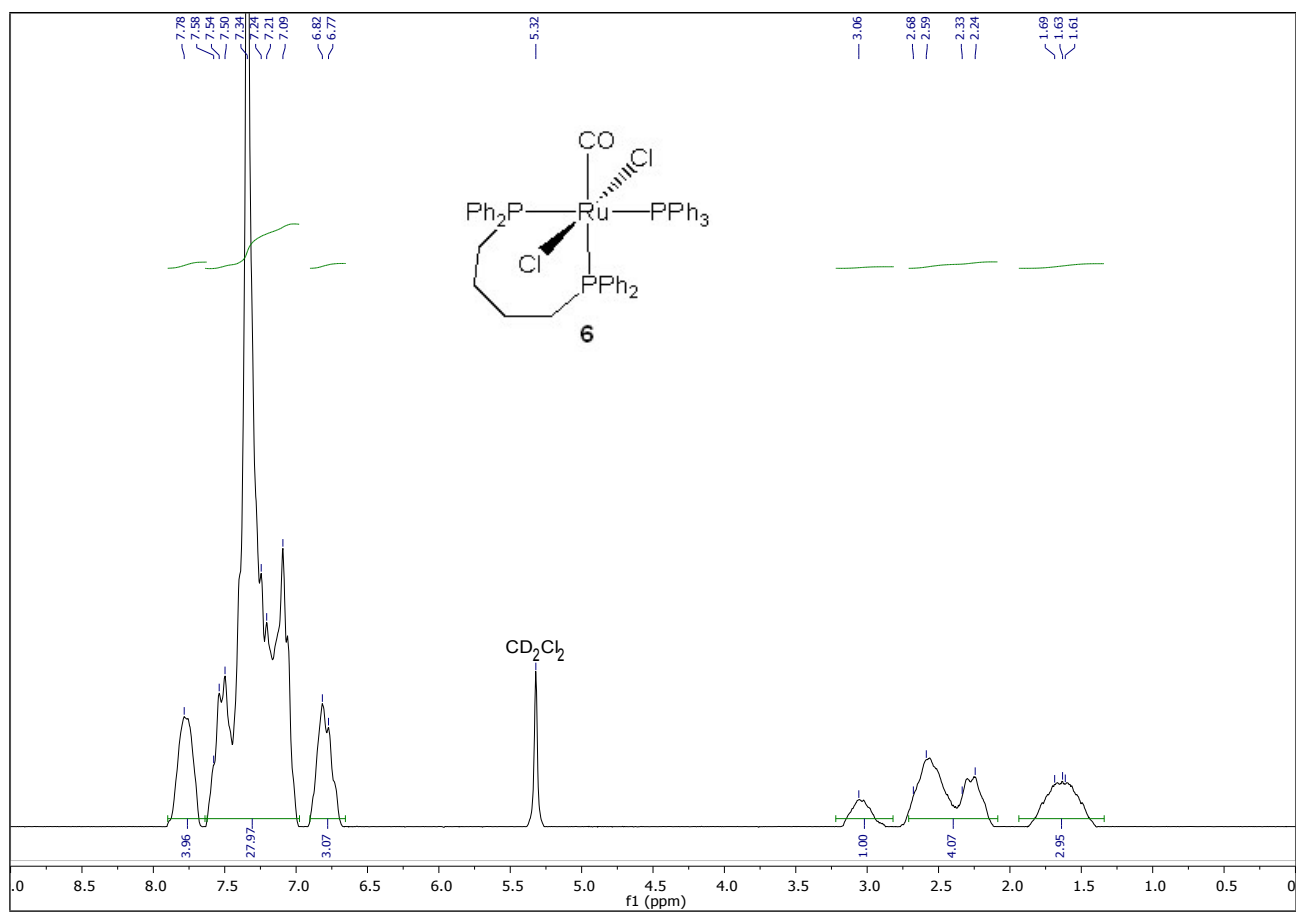




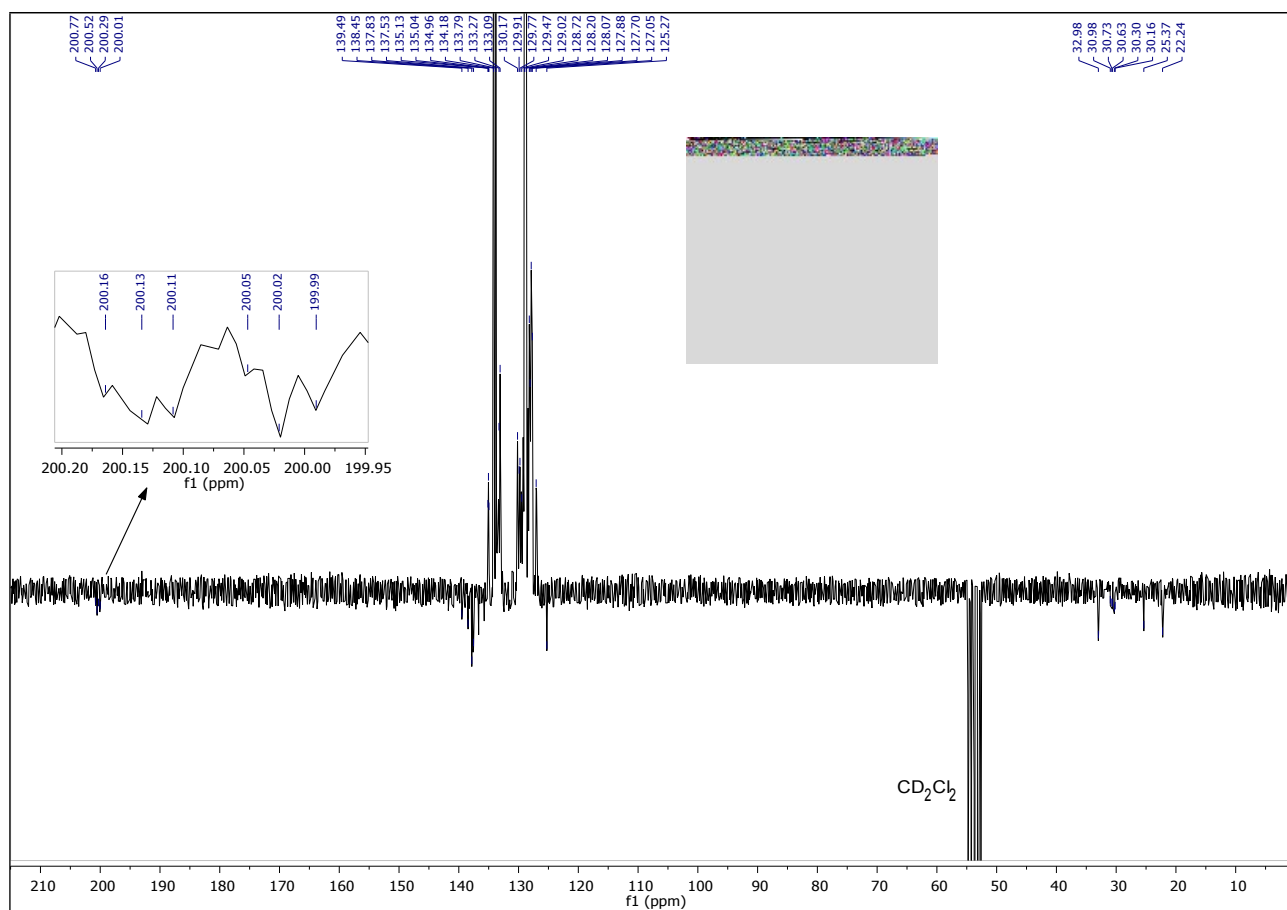
**Figure S20.** Control  $^1\text{H}$  NMR spectrum (200.1 MHz) of the mixture of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{PPh}_3)(\text{ampy})]\text{OAc}$  (**5**) and *trans*- $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{PPh}_3)(\text{ampy})]$  (**B'**) in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$ .



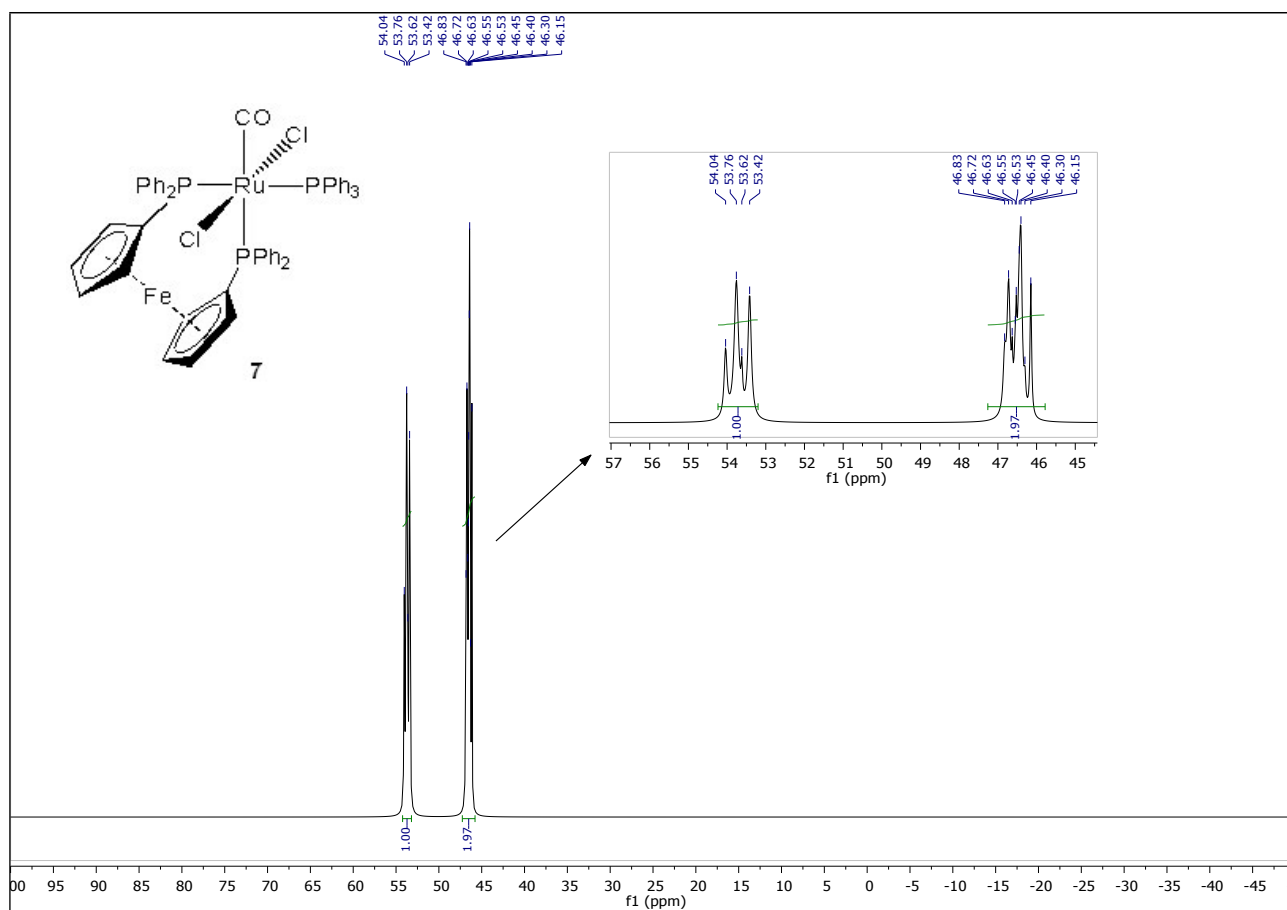
**Figure S21.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of *trans*-[RuCl<sub>2</sub>(CO)(dppb)(PPh<sub>3</sub>)] (6) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.



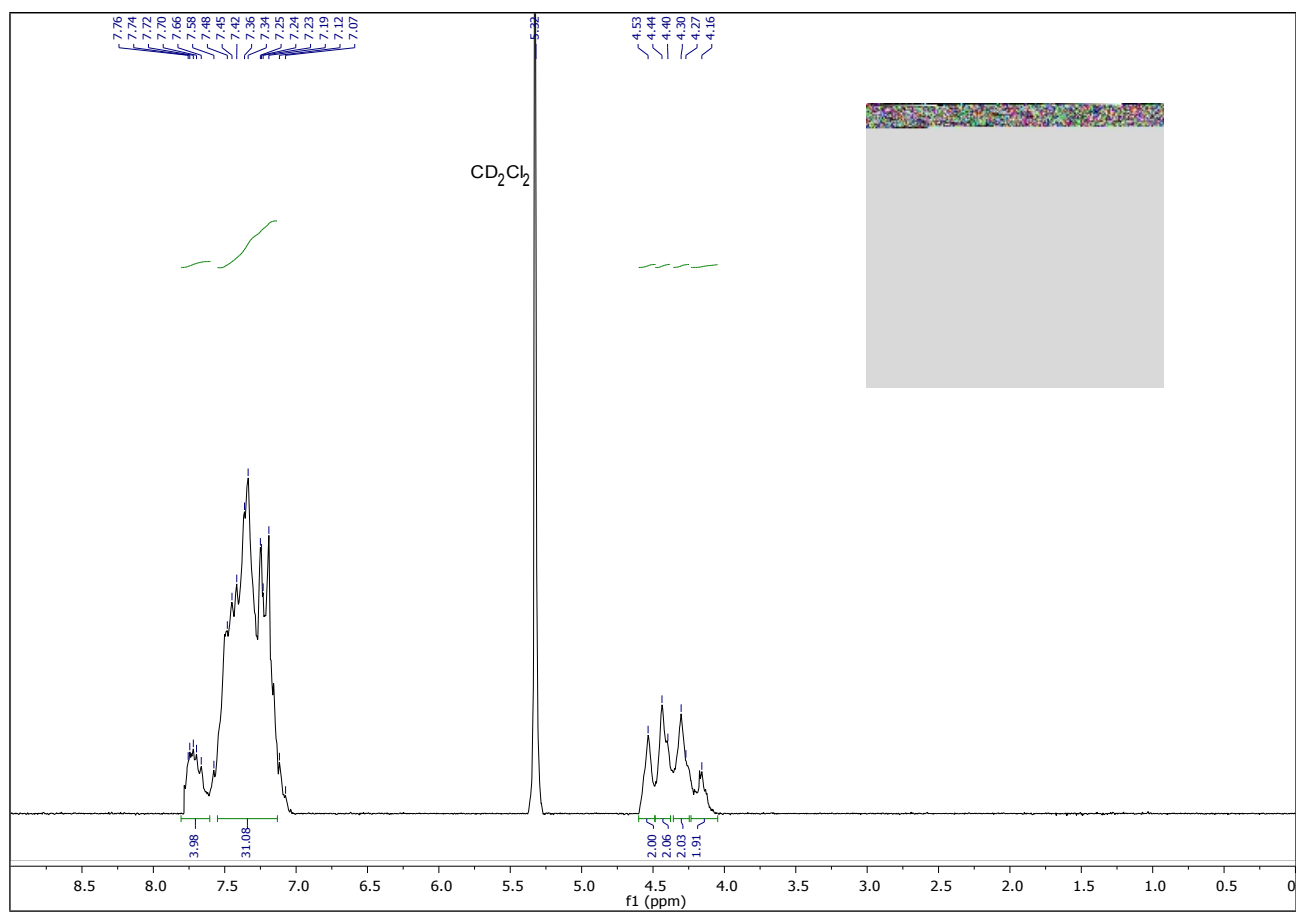
**Figure S22.**  $^1\text{H NMR}$  spectrum (200.1 MHz) of *trans*- $[\text{RuCl}_2(\text{CO})(\text{dppb})(\text{PPh}_3)]$  (**6**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.



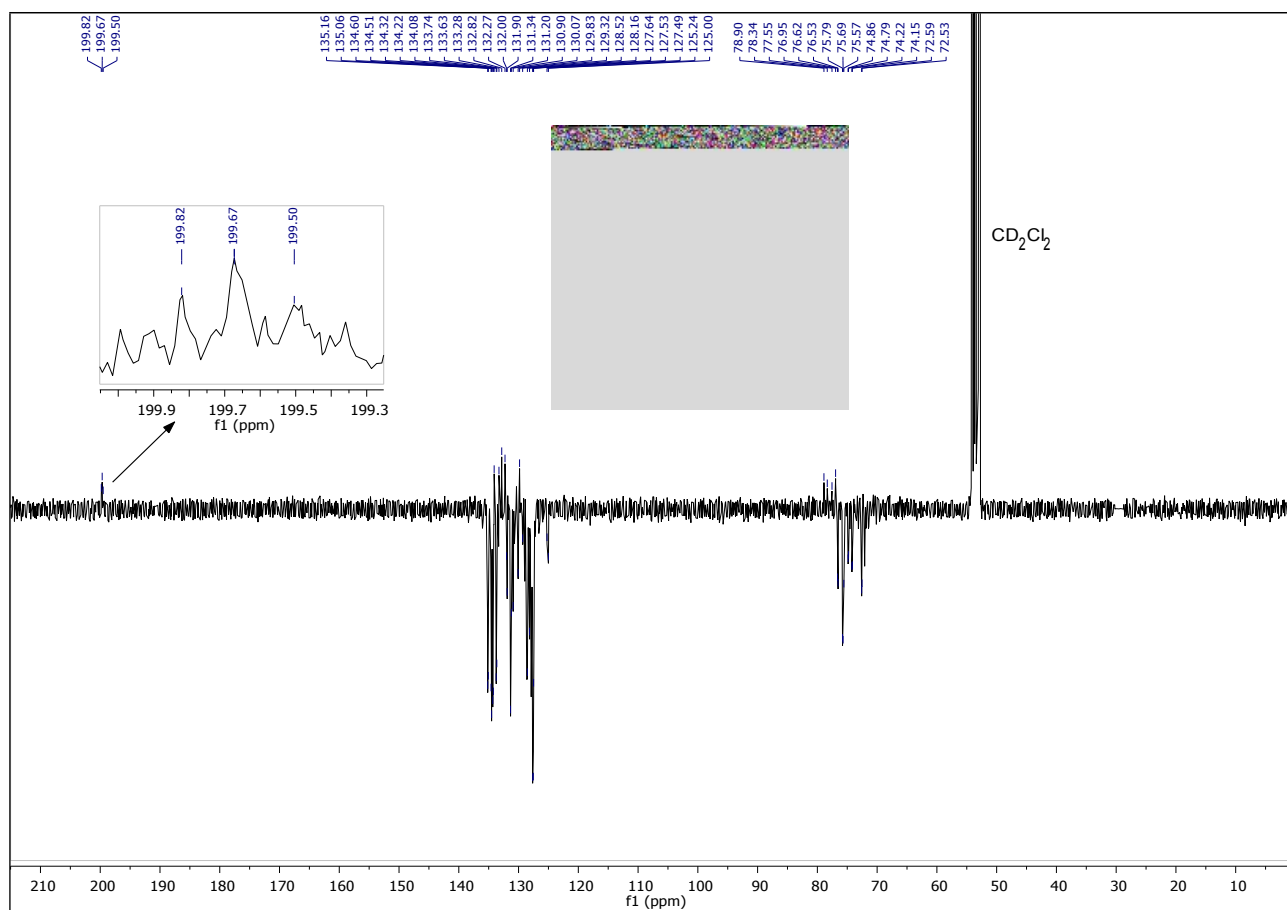
**Figure S23.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum (100.6 MHz) of *trans*-[RuCl<sub>2</sub>(CO)(dppb)(PPh<sub>3</sub>)] (6) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.



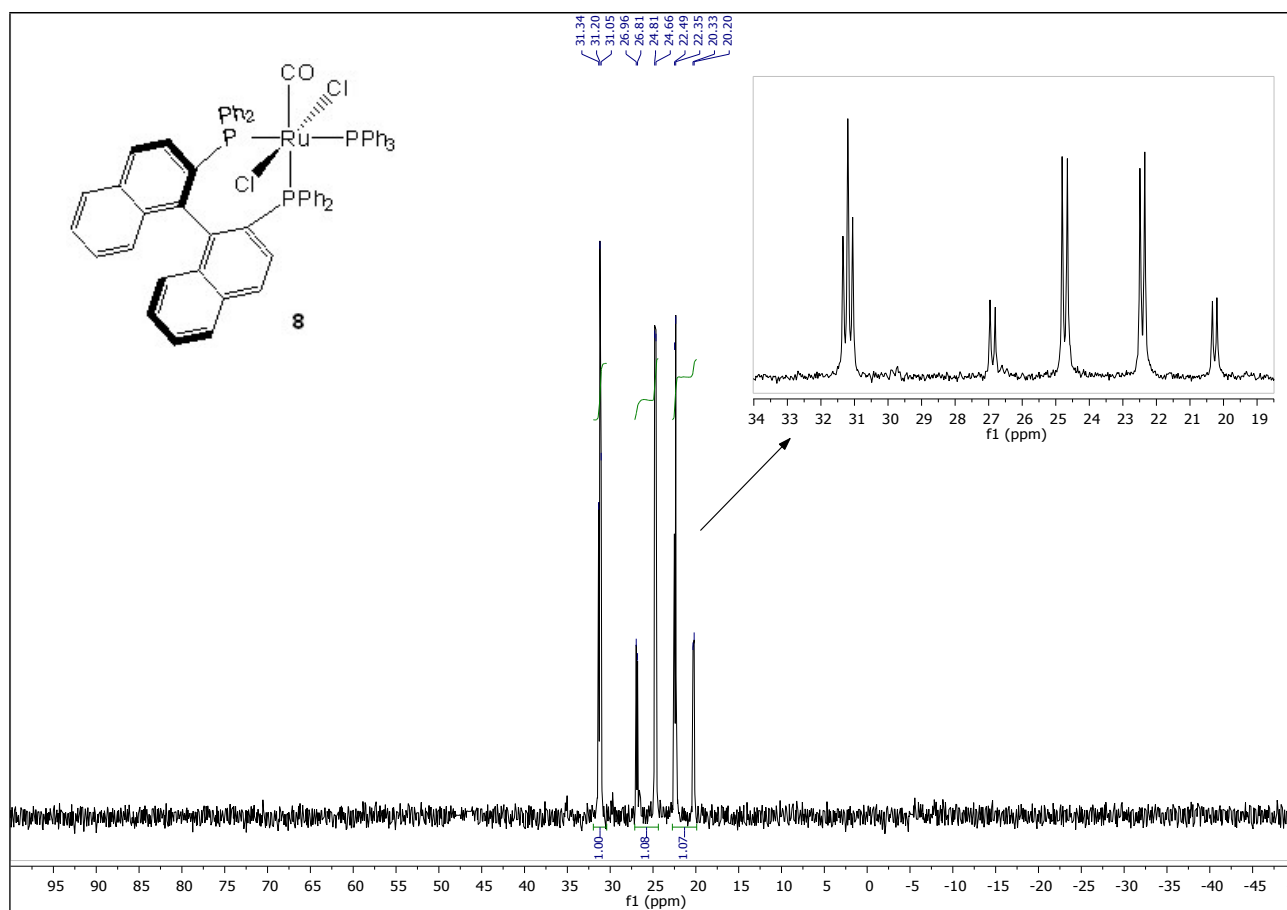
**Figure S24.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $\text{trans-}[\text{RuCl}_2(\text{CO})(\text{dppf})(\text{PPh}_3)]$  (7) in  $\text{CD}_2\text{Cl}_2$  at  $20\text{ }^\circ\text{C}$ .



**Figure S25.**  $^1\text{H}$  NMR spectrum (200.1 MHz) of *trans*-[RuCl<sub>2</sub>(CO)(dppf)(PPh<sub>3</sub>)] (7) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.

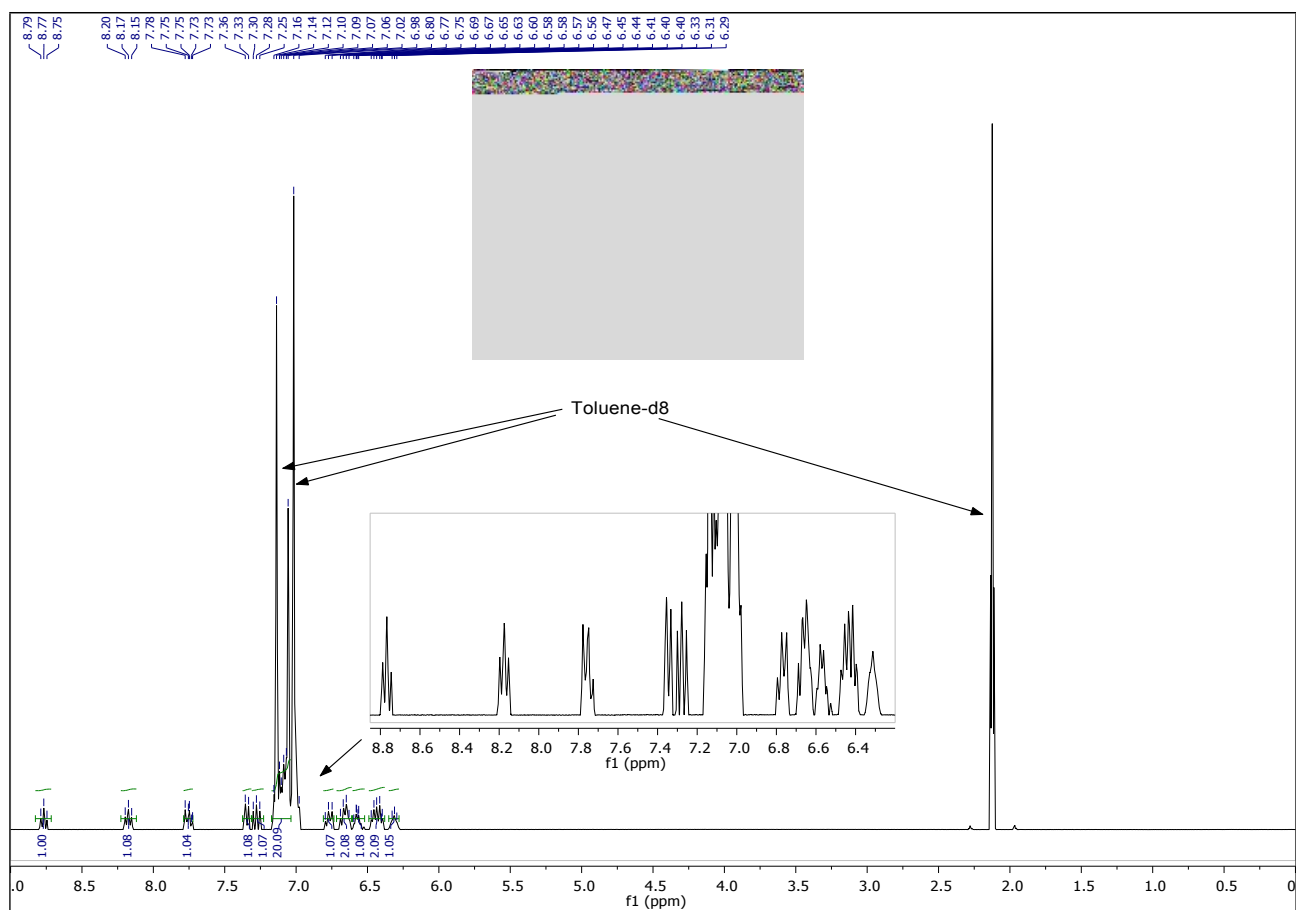


**Figure S26.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum (100.6 MHz) of *trans*-[RuCl<sub>2</sub>(CO)(dppf)(PPh<sub>3</sub>)] (**7**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.

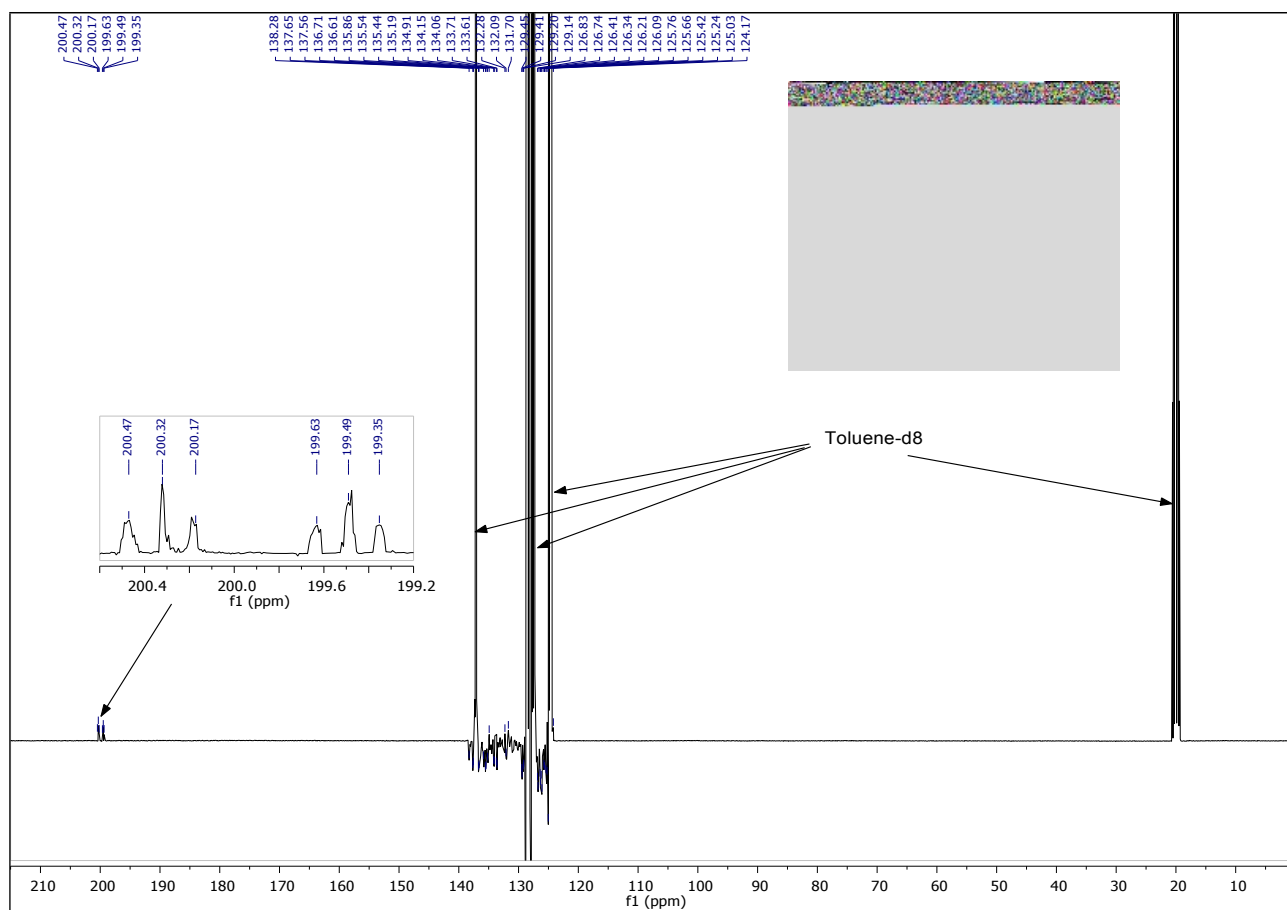


**Figure S27.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (162.0 MHz) of *trans*-[RuCl<sub>2</sub>(CO)((*R*)-BINAP)(PPh<sub>3</sub>)] (**8**) in [D<sub>8</sub>]toluene at 20 °C.

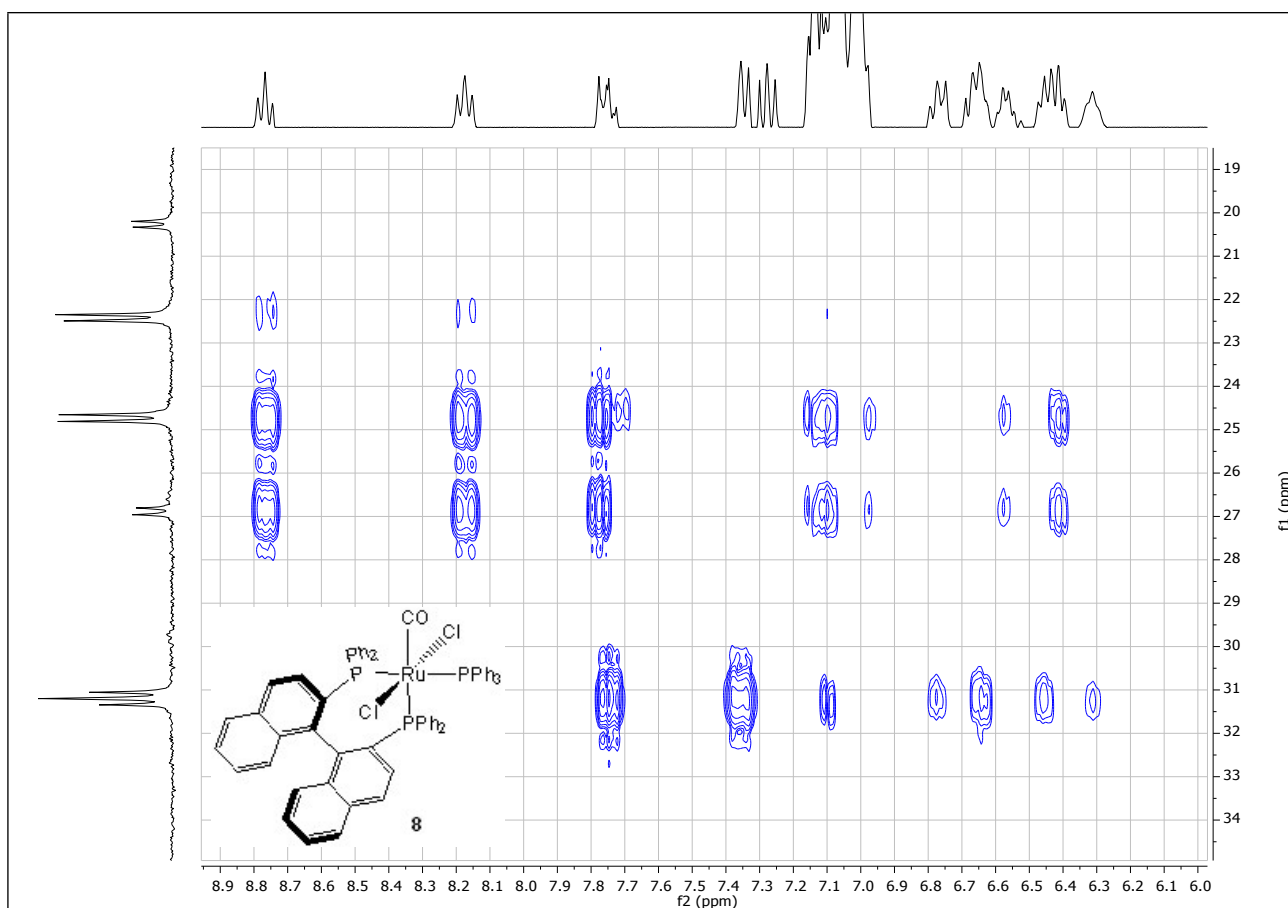




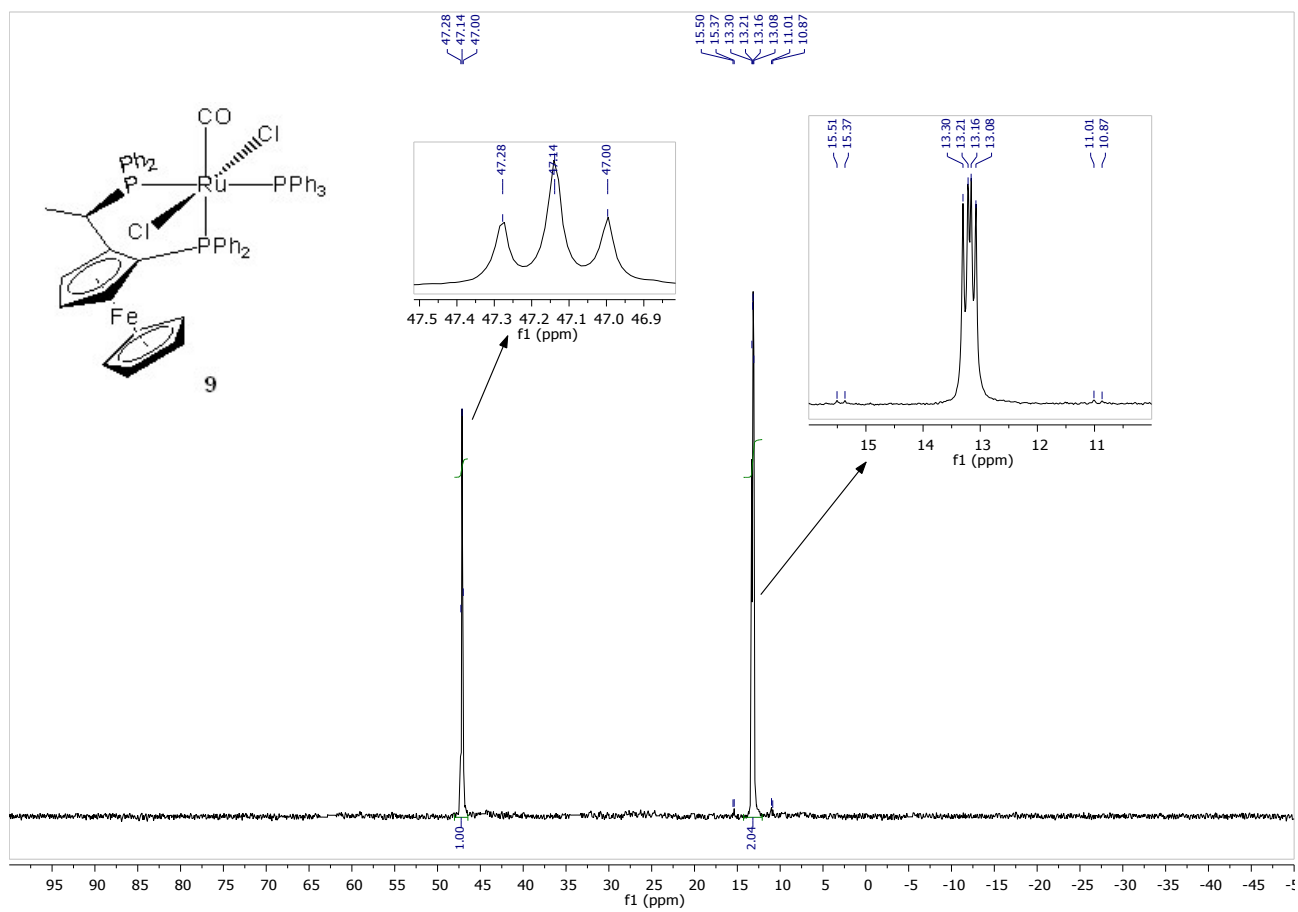
**Figure S28.**  $^1\text{H}$  NMR spectrum (400.1 MHz) of  $\text{trans-}[\text{RuCl}_2(\text{CO})((R)\text{-BINAP})(\text{PPh}_3)]$  (**8**) in  $[\text{D}_8]\text{toluene}$  at  $20\text{ }^\circ\text{C}$ .



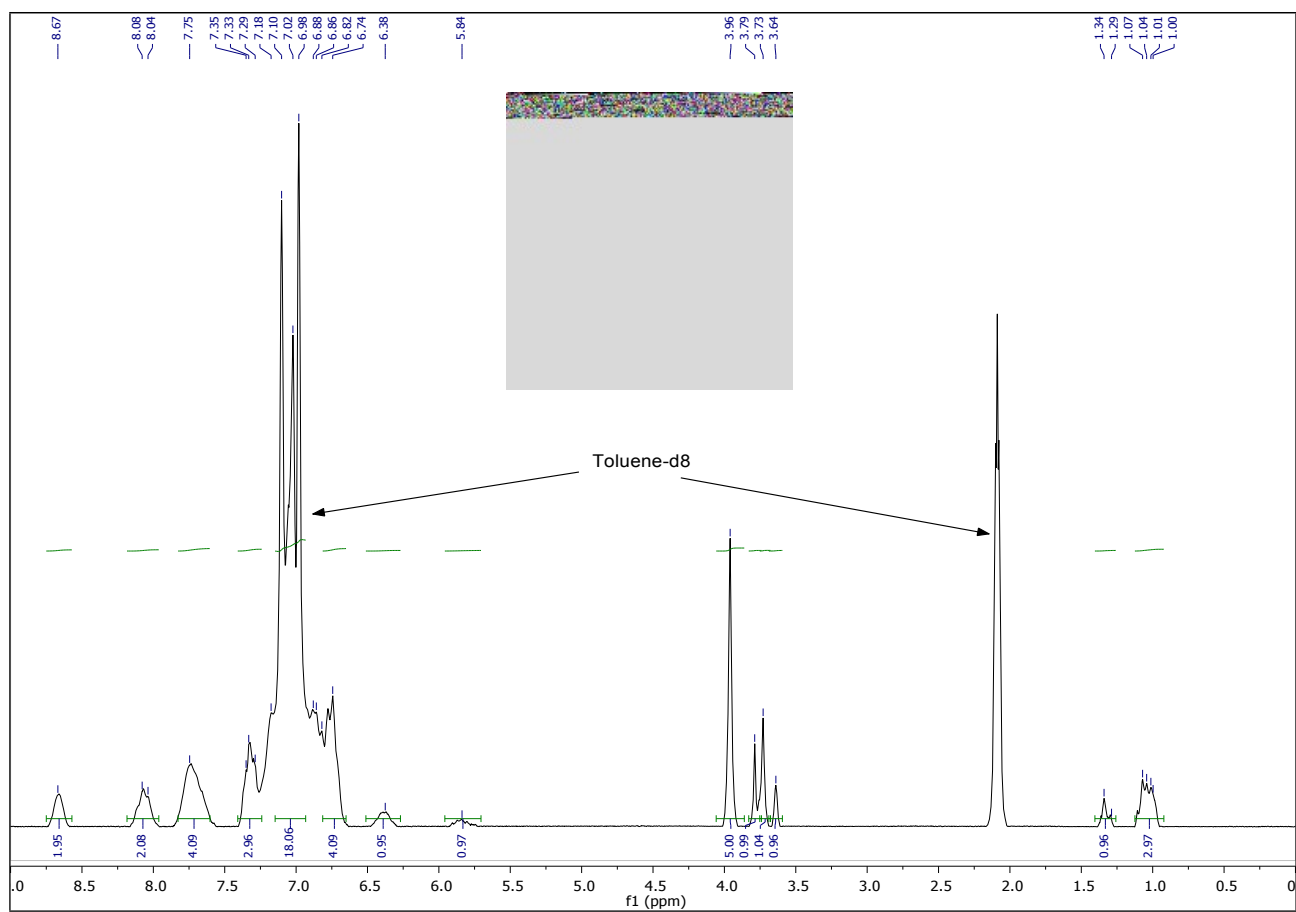
**Figure S29.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum (100.6 MHz) of *trans*-[RuCl<sub>2</sub>(CO)((*R*)-BINAP)(PPh<sub>3</sub>)] (**8**) in [D<sub>8</sub>]toluene at 20 °C.



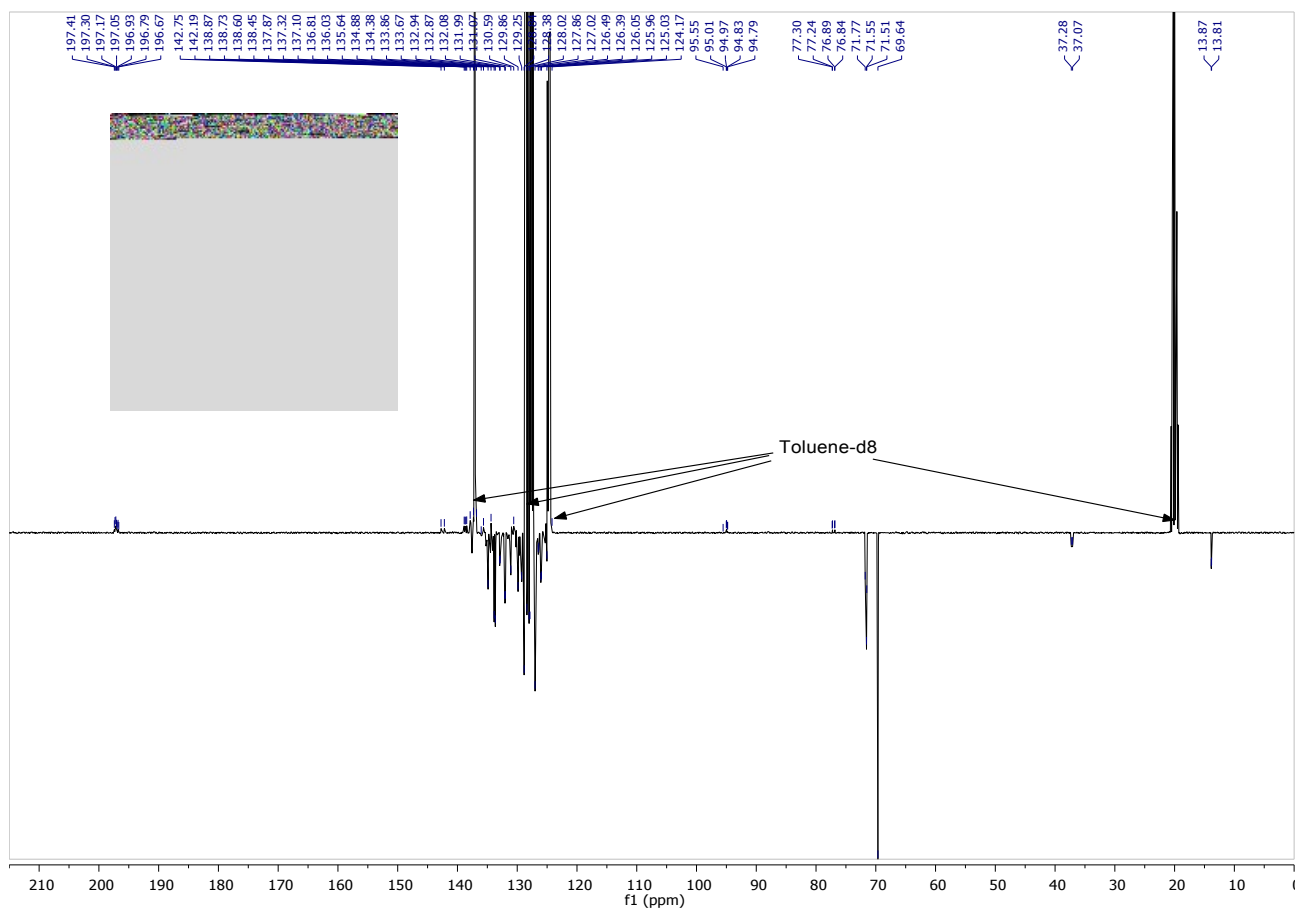
**Figure S30.**  $^{31}\text{P}$ - $^1\text{H}$  HMBC 2D NMR spectrum of *trans*-[RuCl<sub>2</sub>(CO)((*R*)-BINAP)(PPh<sub>3</sub>)] (**8**) in [D<sub>8</sub>]toluene at 20 °C.



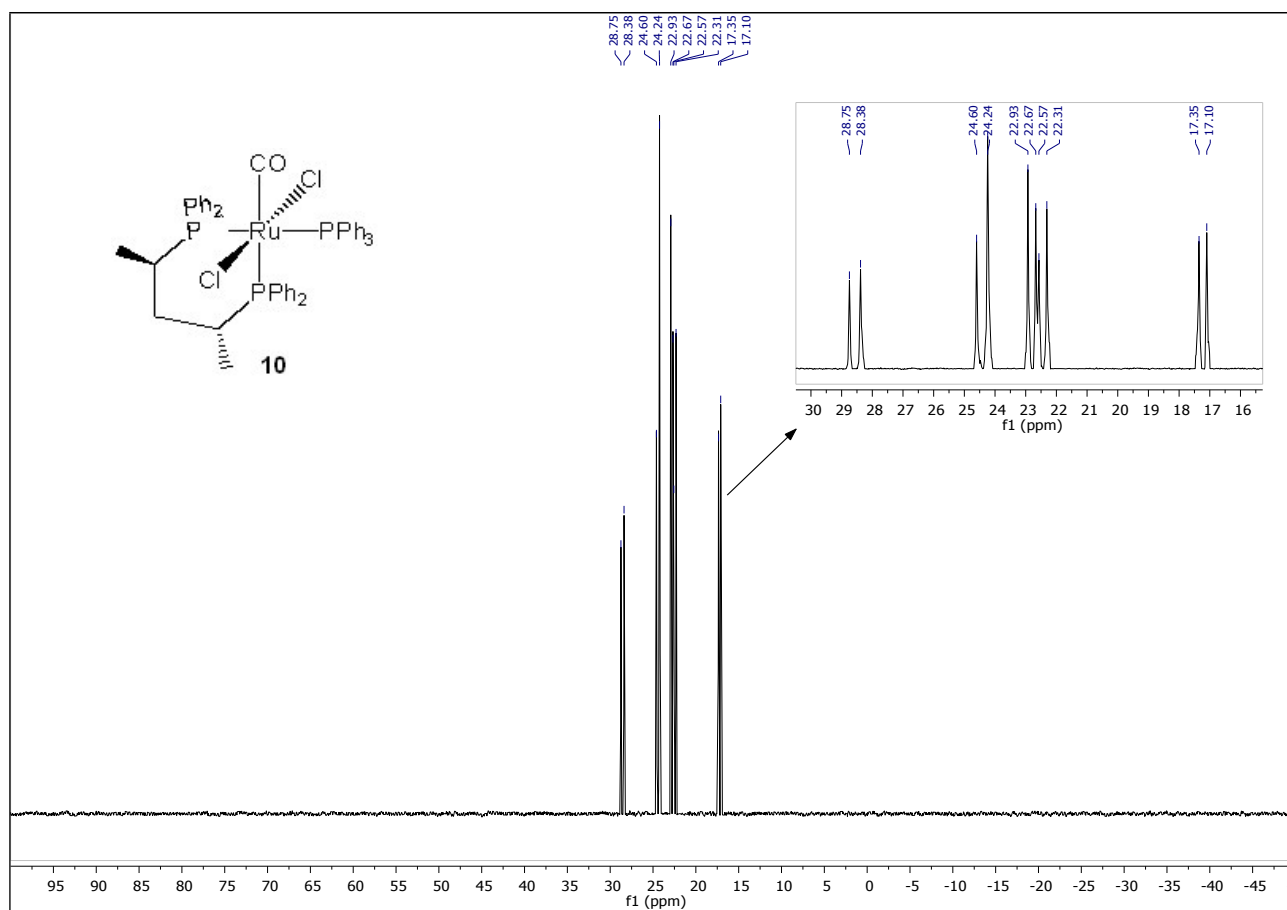
**Figure S31.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (162.0 MHz) of *trans*- $[\text{RuCl}_2(\text{CO})((S,R)\text{-Josiphos})(\text{PPh}_3)]$  (**9**) in  $[\text{D}_8]\text{toluene}$  at  $20\text{ }^\circ\text{C}$ .



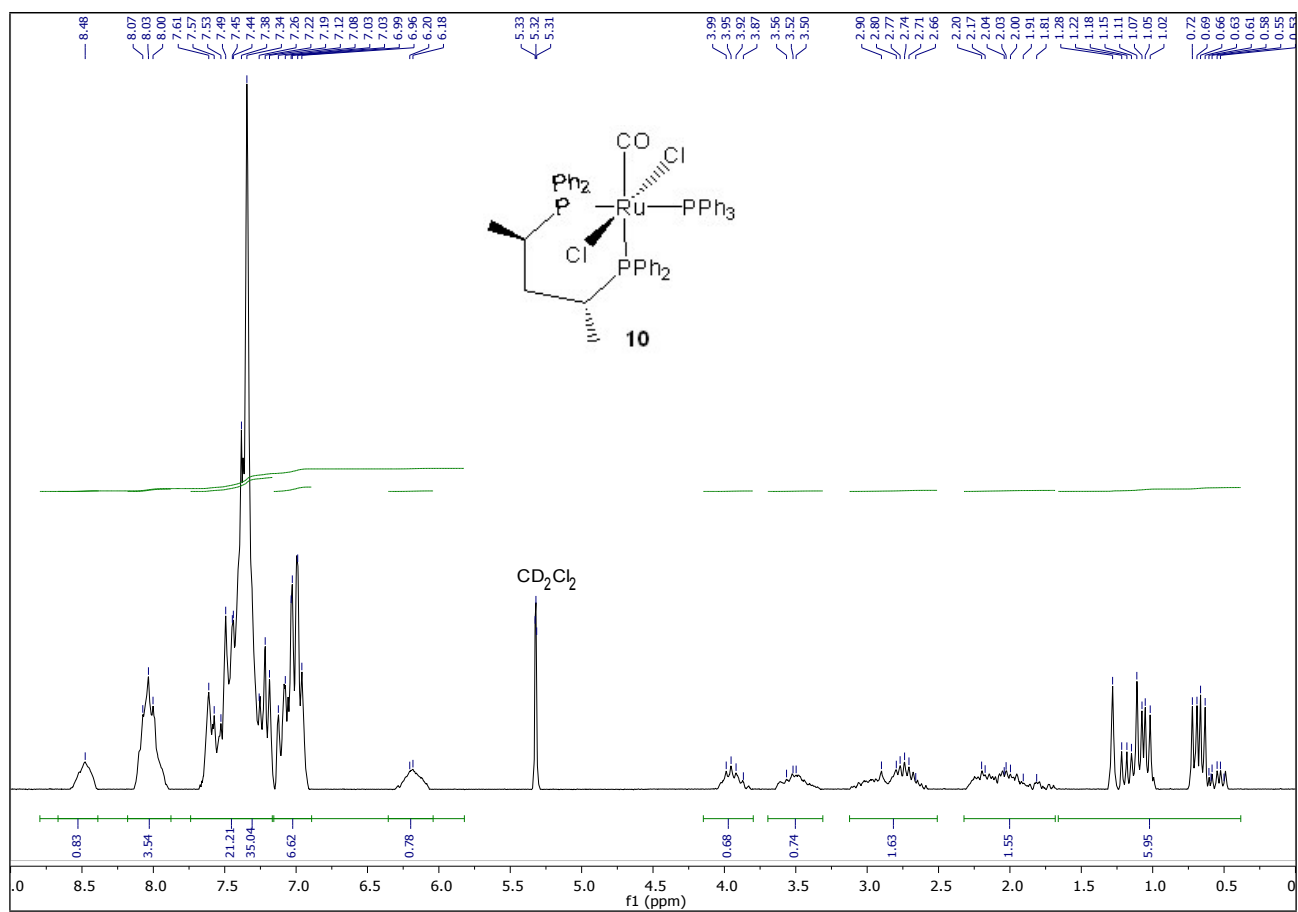
**Figure S32.** <sup>1</sup>H NMR spectrum (400.1 MHz) of *trans*-[RuCl<sub>2</sub>(CO)((*S,R*)-Josiphos)(PPh<sub>3</sub>)] (**9**) in [D<sub>8</sub>]toluene at 20 °C.



**Figure S33.**  $^{13}\text{C}\{^1\text{H}\}$  DEPTQ NMR spectrum (100.6 MHz) of *trans*-[RuCl<sub>2</sub>(CO)((*S,R*)-Josiphos)(PPh<sub>3</sub>)] (**9**) in [D<sub>8</sub>]toluene at 20 °C.

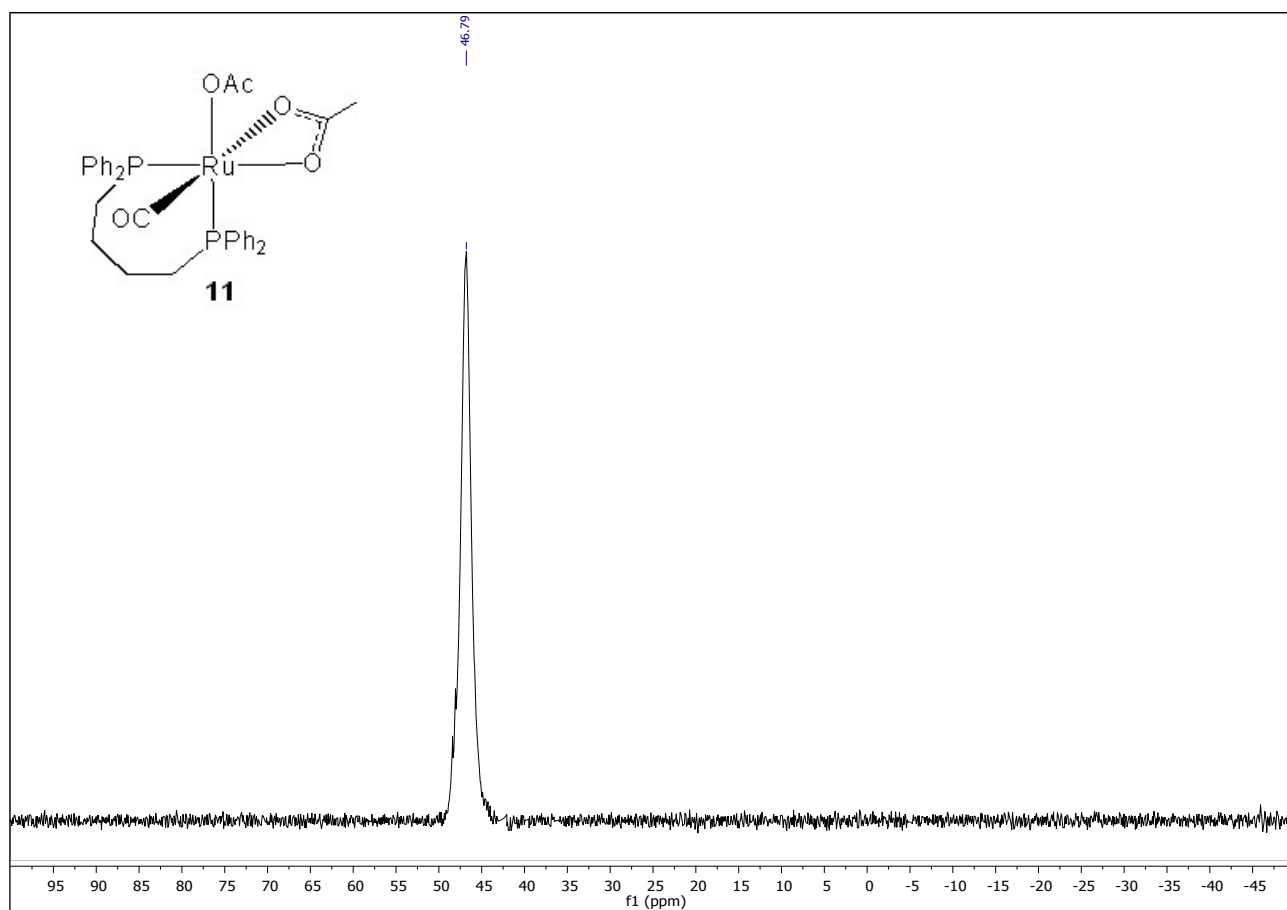


**Figure S34.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of *trans*- $[\text{RuCl}_2(\text{CO})((R,R)\text{-Skewphos})(\text{PPh}_3)]$  (**10**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.

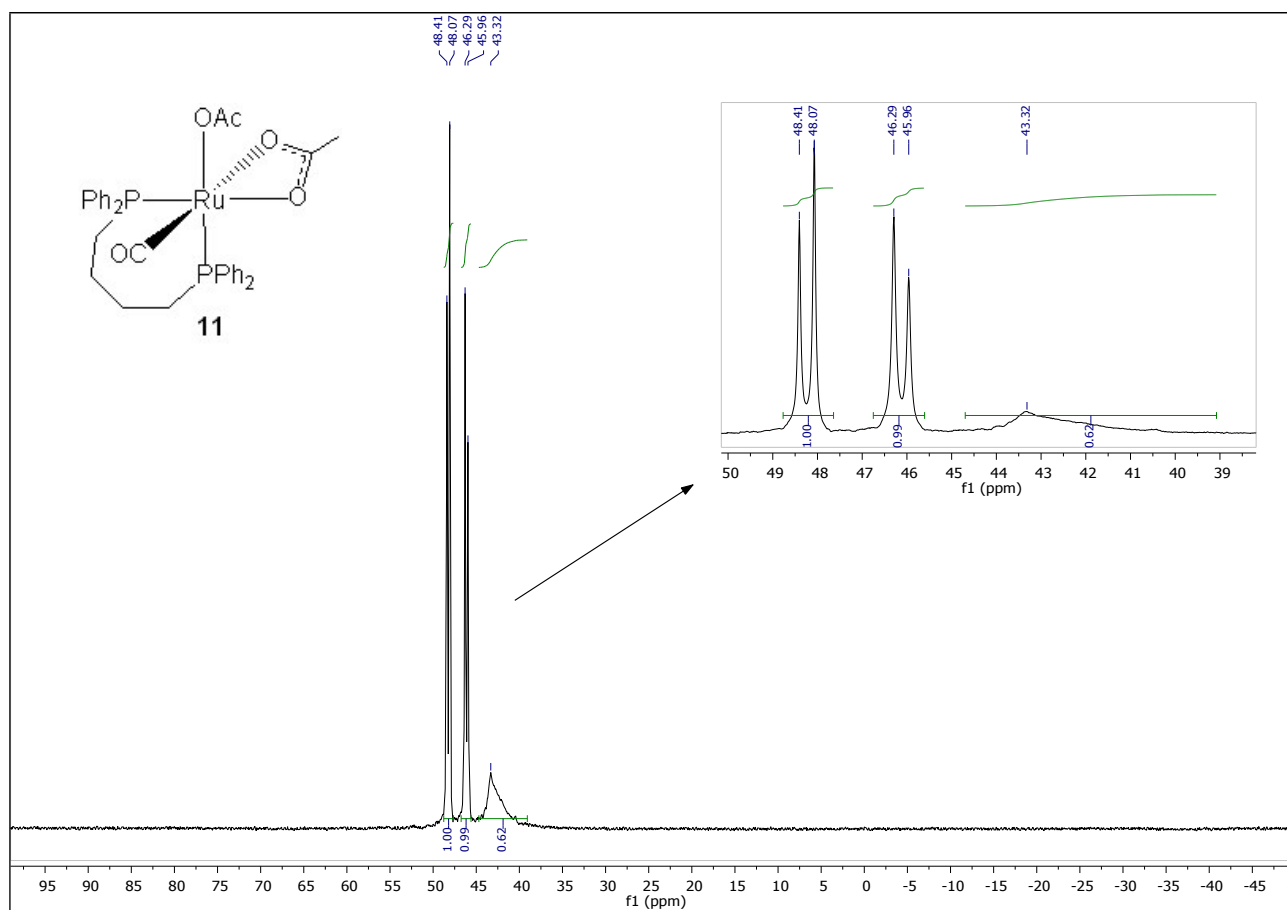


**Figure S35.**  $^1\text{H NMR}$  spectrum (200.1 MHz) of  $\text{trans-[RuCl}_2(\text{CO})((R,R)\text{-Skewphos})(\text{PPh}_3)]$  (**10**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.

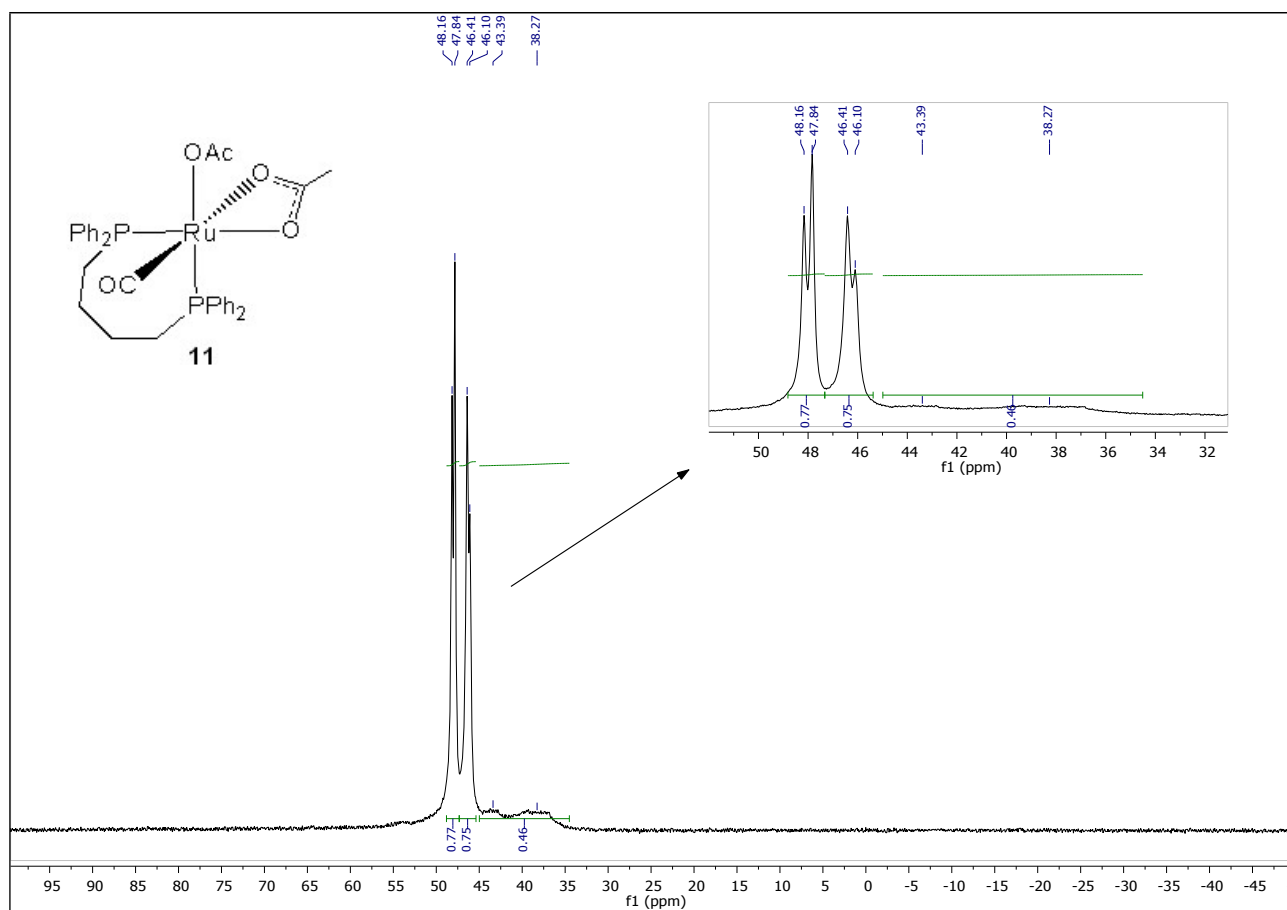




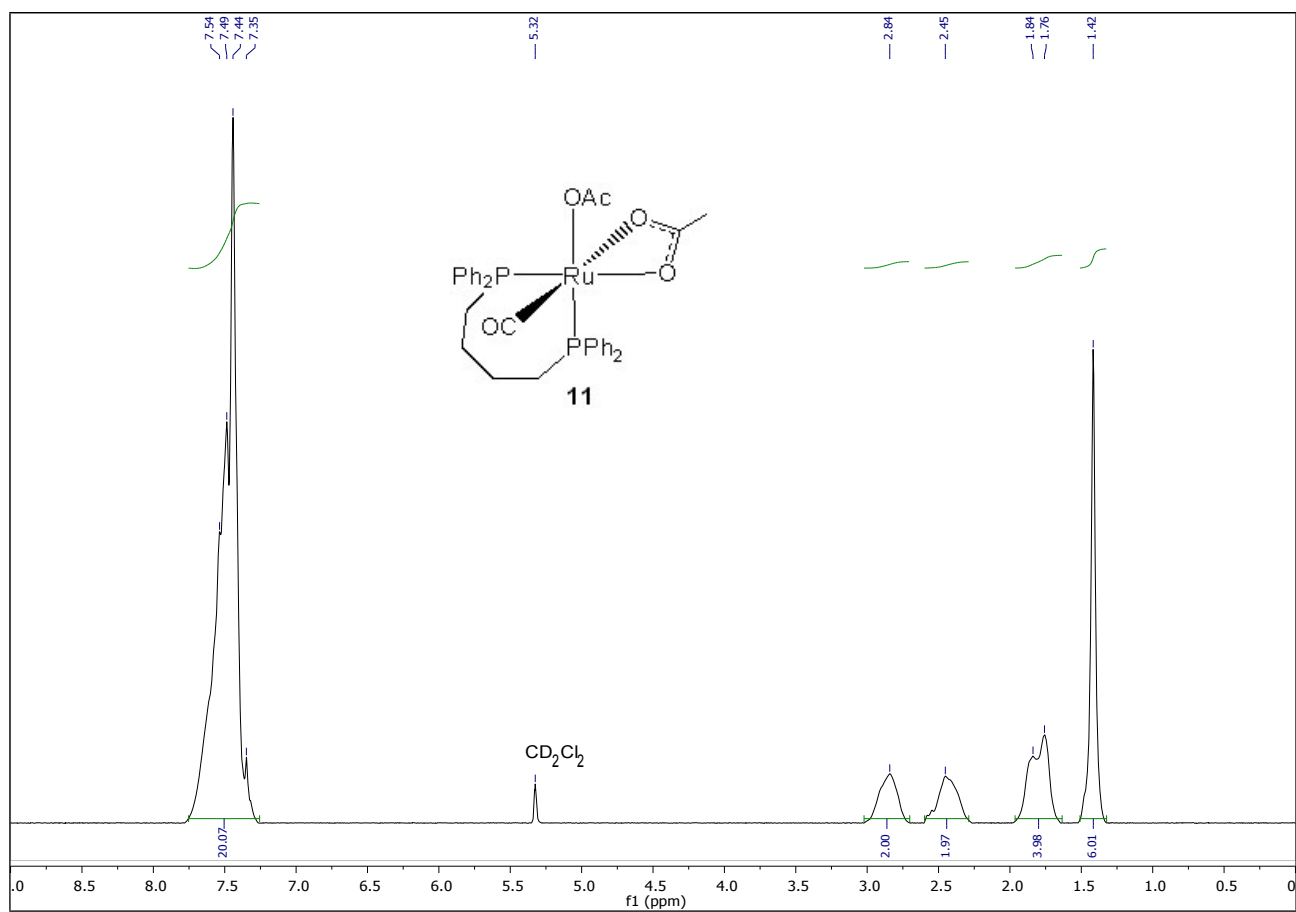
**Figure S36.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppb})]$  (**11**) in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$ .



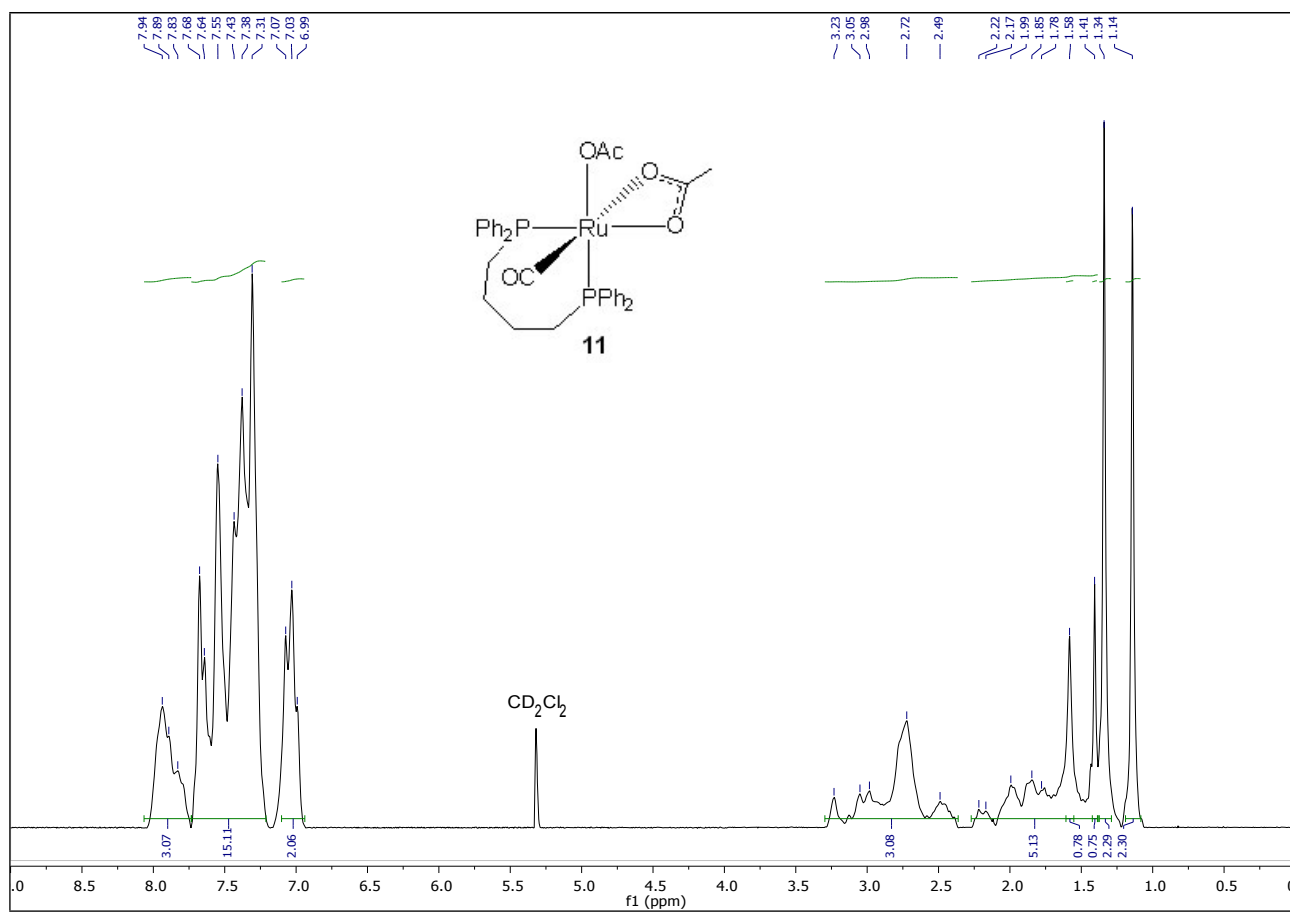
**Figure S37.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppb})]$  (**11**) in  $\text{CD}_2\text{Cl}_2$  at  $-60\text{ }^\circ\text{C}$ .



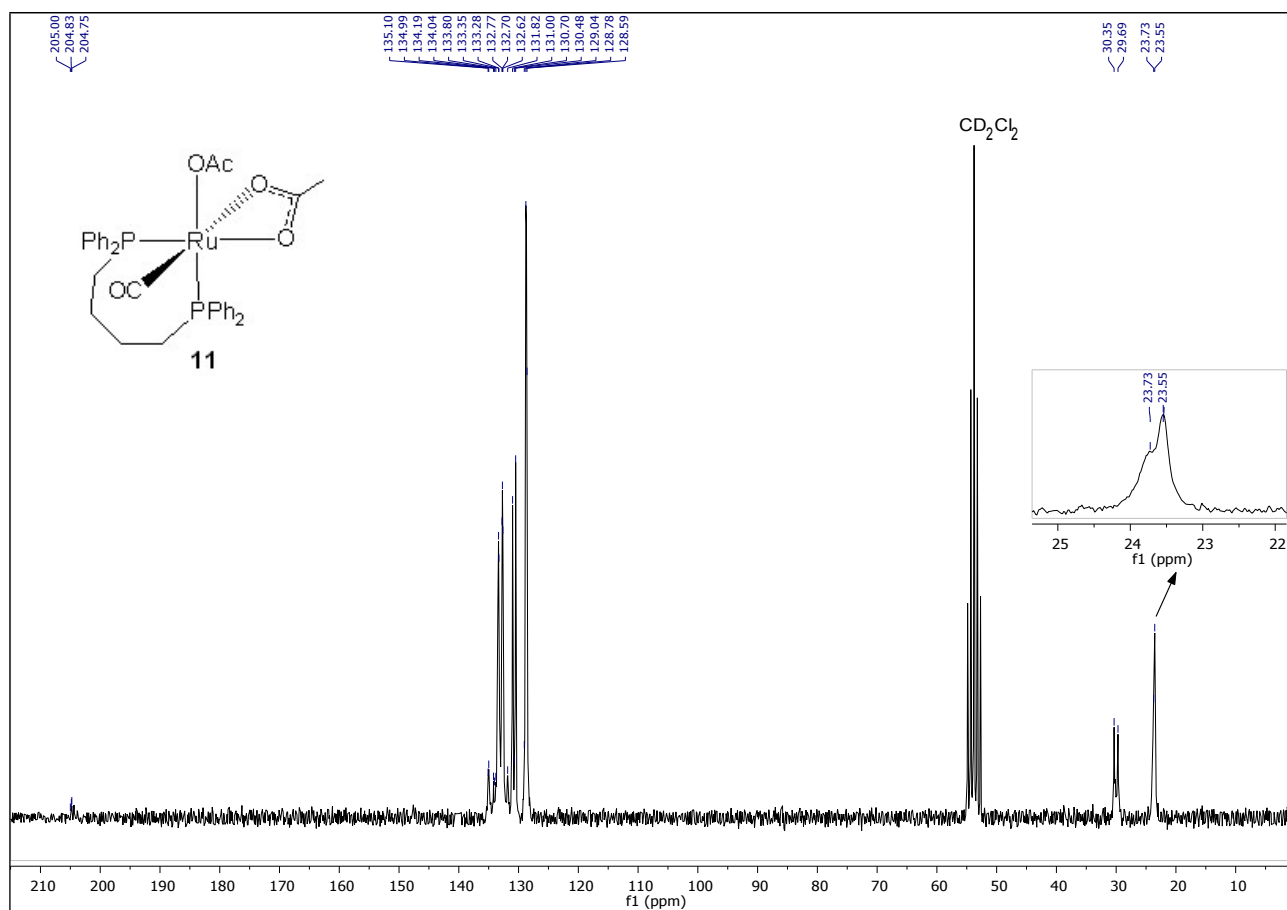
**Figure S38.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum (81.0 MHz) of [Ru(OAc)<sub>2</sub>(CO)(dppb)] (**11**) in CD<sub>2</sub>Cl<sub>2</sub> at -80 °C.



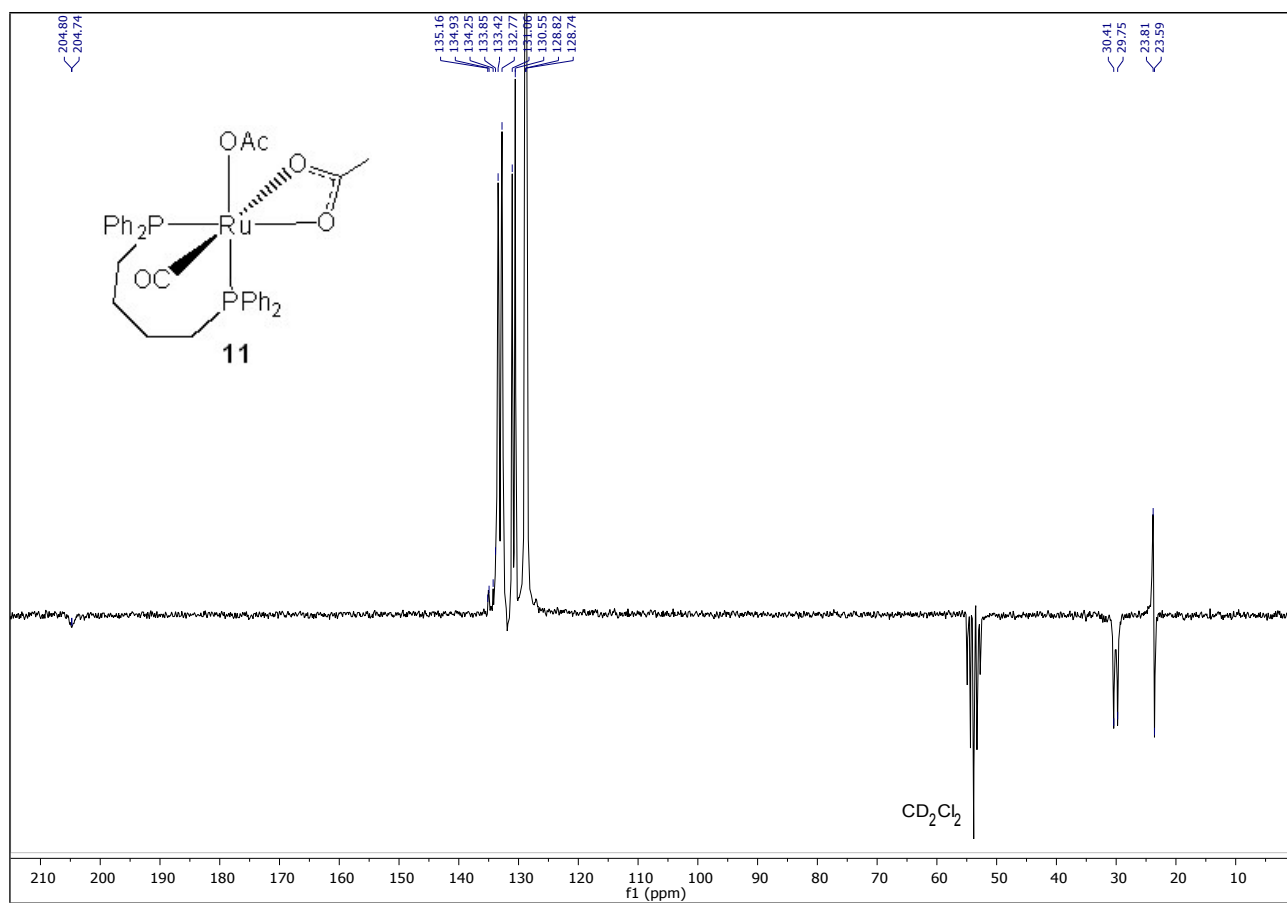
**Figure S39.**  $^1\text{H}$  NMR spectrum (200.1 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppb})]$  (11) in  $\text{CD}_2\text{Cl}_2$  at  $20\text{ }^\circ\text{C}$ .



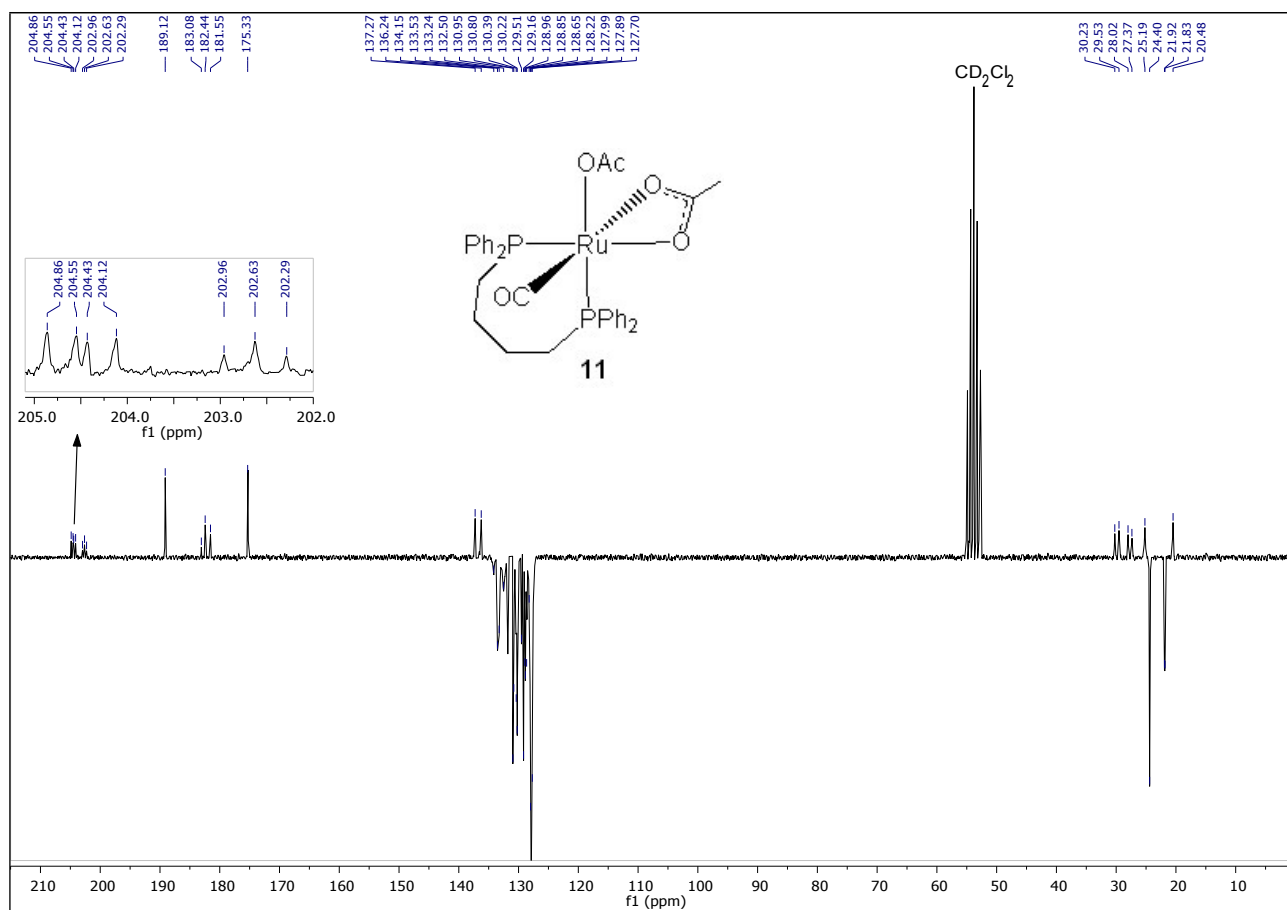
**Figure S40.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [Ru(OAc)<sub>2</sub>(CO)(dppb)] (**11**) in CD<sub>2</sub>Cl<sub>2</sub> at -80 °C.



**Figure S41.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppb})]$  (**11**) in  $\text{CD}_2\text{Cl}_2$  at  $20\text{ }^\circ\text{C}$ .

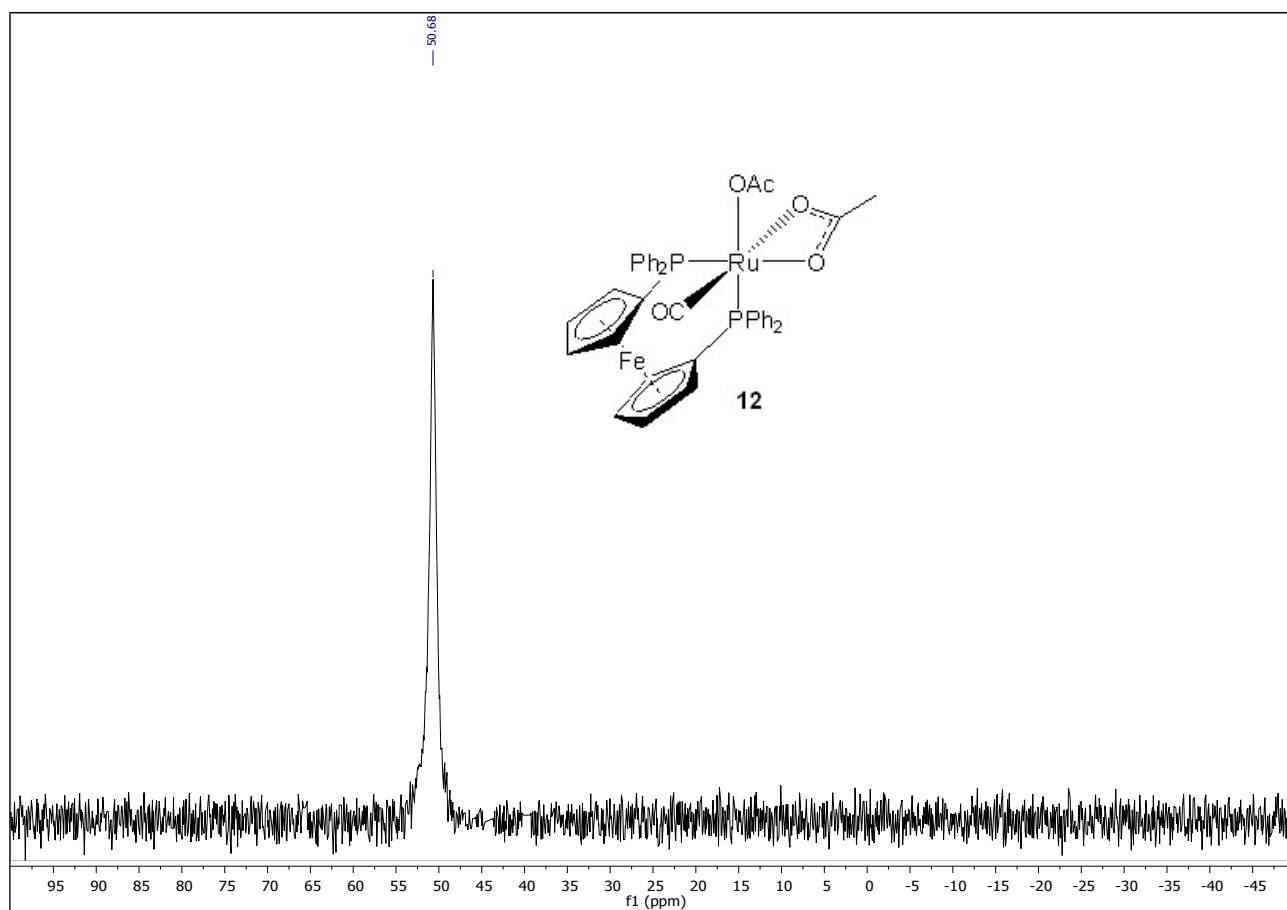


**Figure S42.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppb})]$  (**11**) in  $\text{CD}_2\text{Cl}_2$  at  $20\text{ }^\circ\text{C}$ .

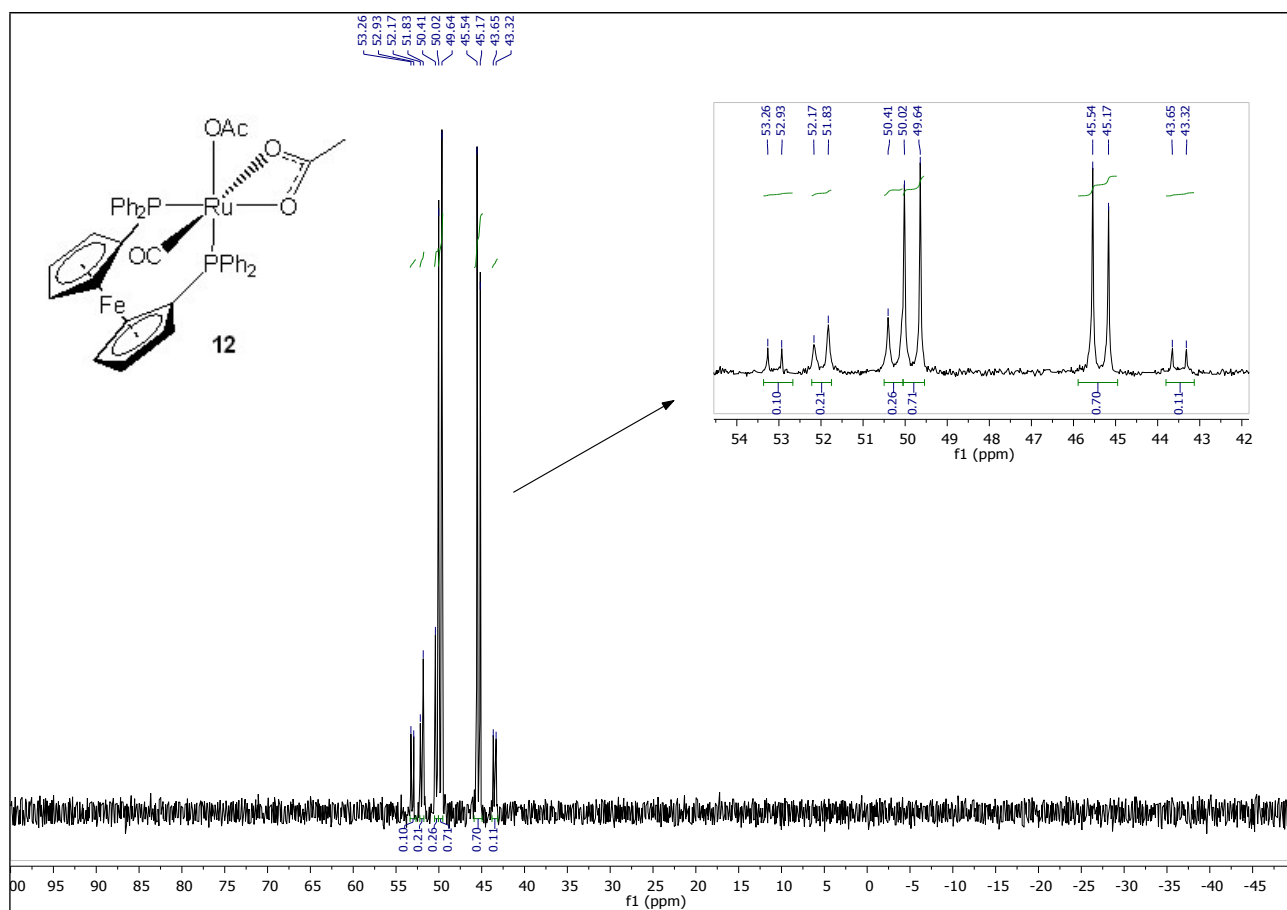


**Figure S43.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppb})]$  (**11**) in  $\text{CD}_2\text{Cl}_2$  at  $-80\text{ }^\circ\text{C}$ .

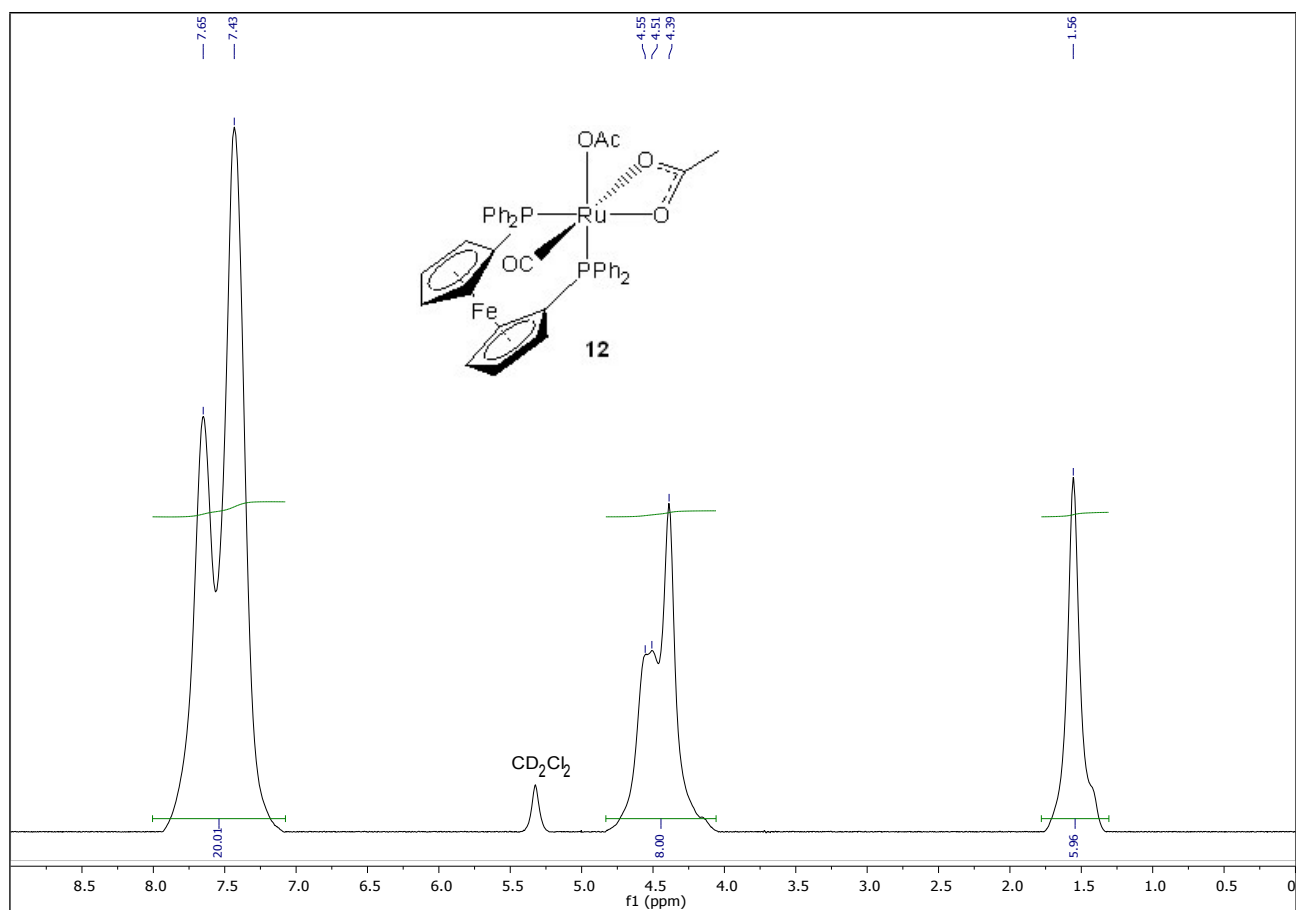




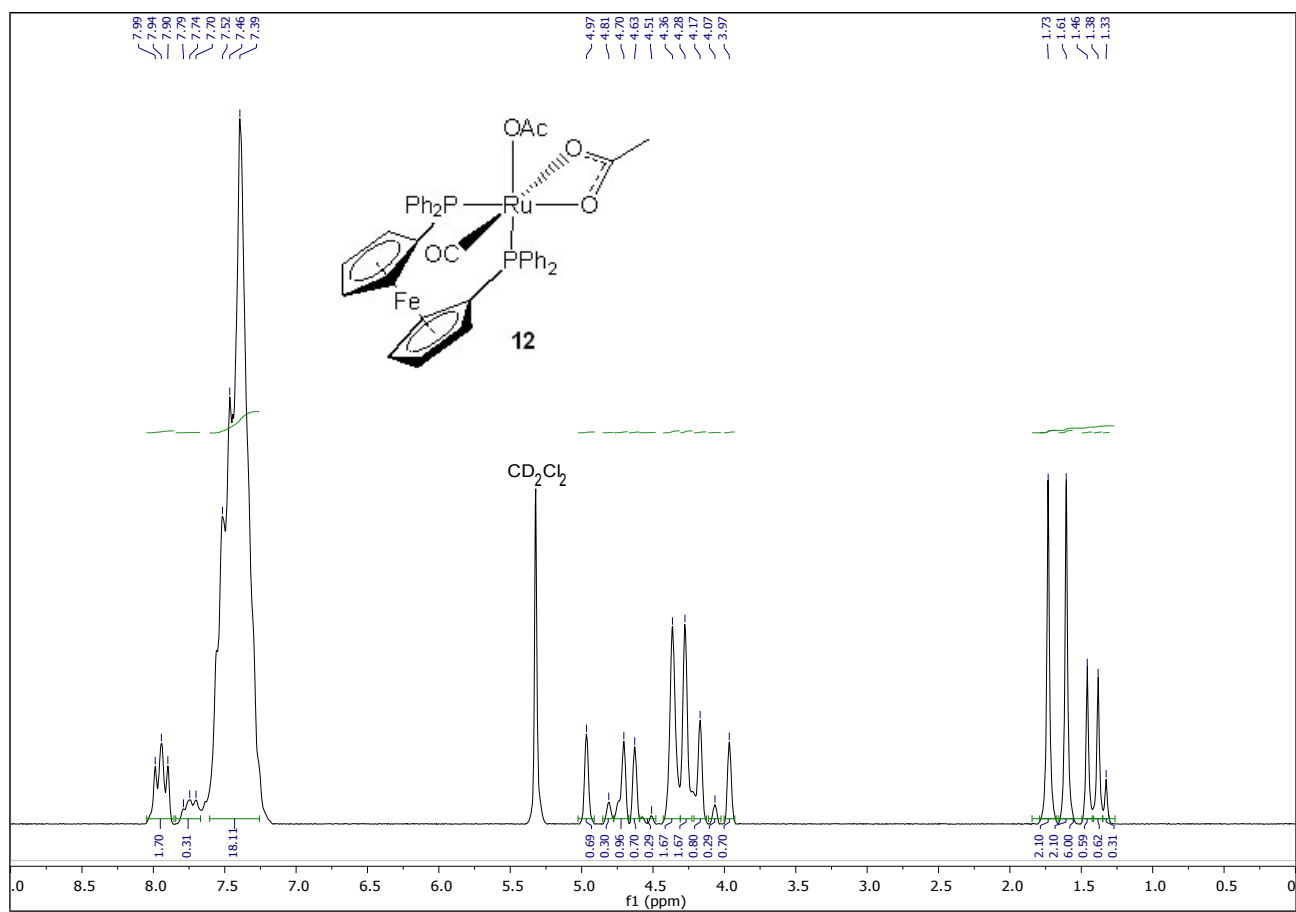
**Figure S44.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppf})]$  (**12**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.



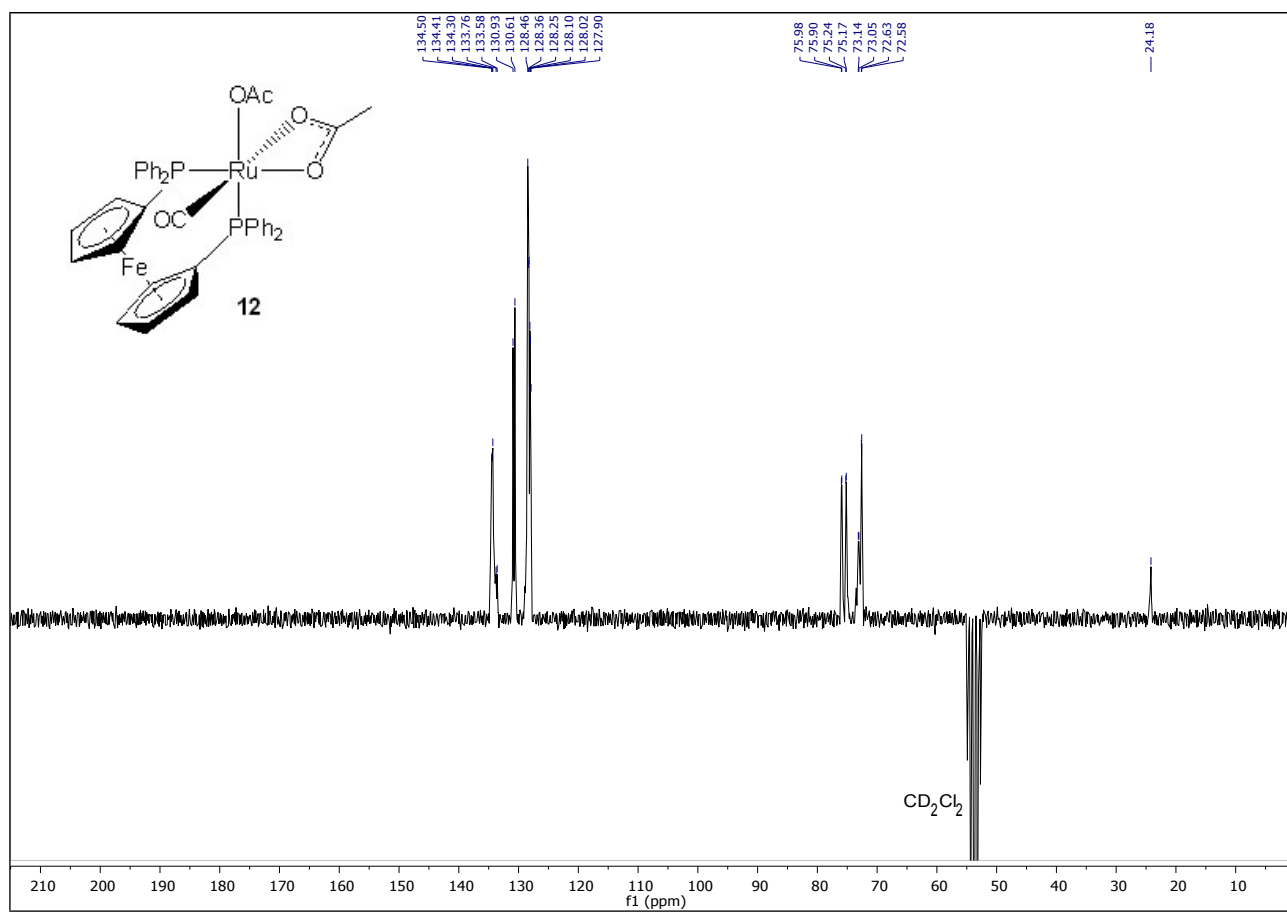
**Figure S45.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppf})]$  (**12**) in  $\text{CD}_2\text{Cl}_2$  at  $-70$   $^\circ\text{C}$ .



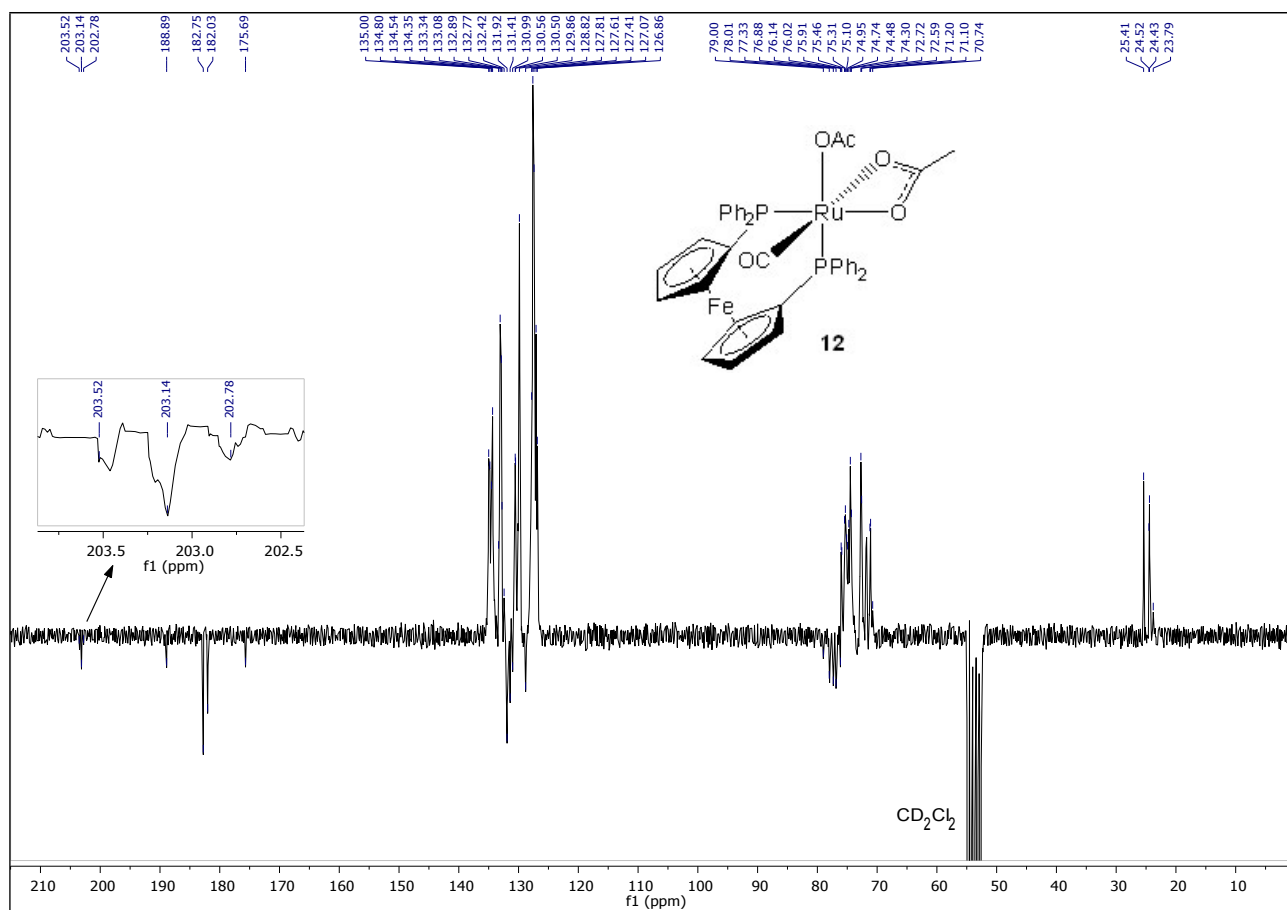
**Figure S46.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [Ru(OAc)<sub>2</sub>(CO)(dppf)] (**12**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.



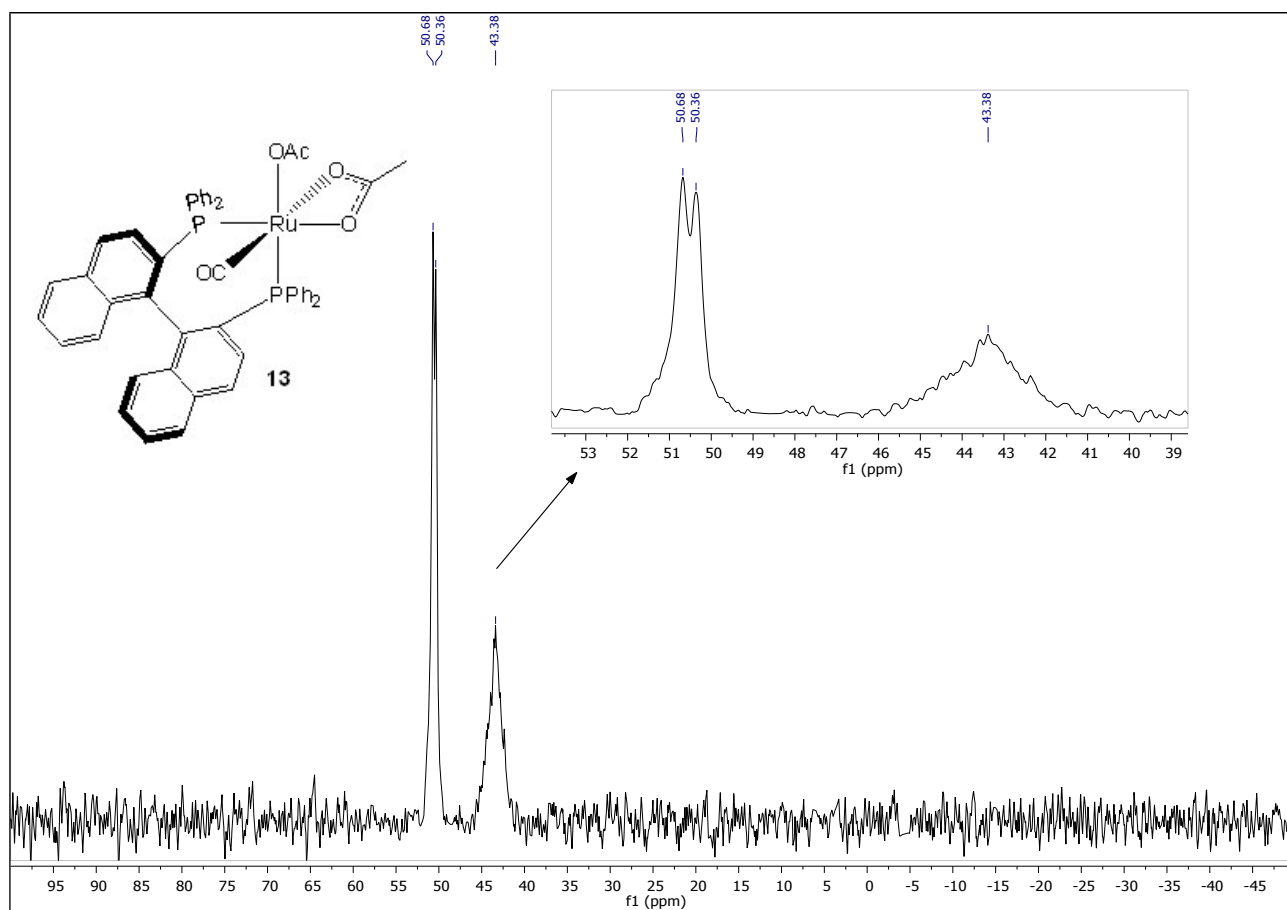
**Figure S47.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [Ru(OAc)<sub>2</sub>(CO)(dppf)] (**12**) in CD<sub>2</sub>Cl<sub>2</sub> at -70 °C.



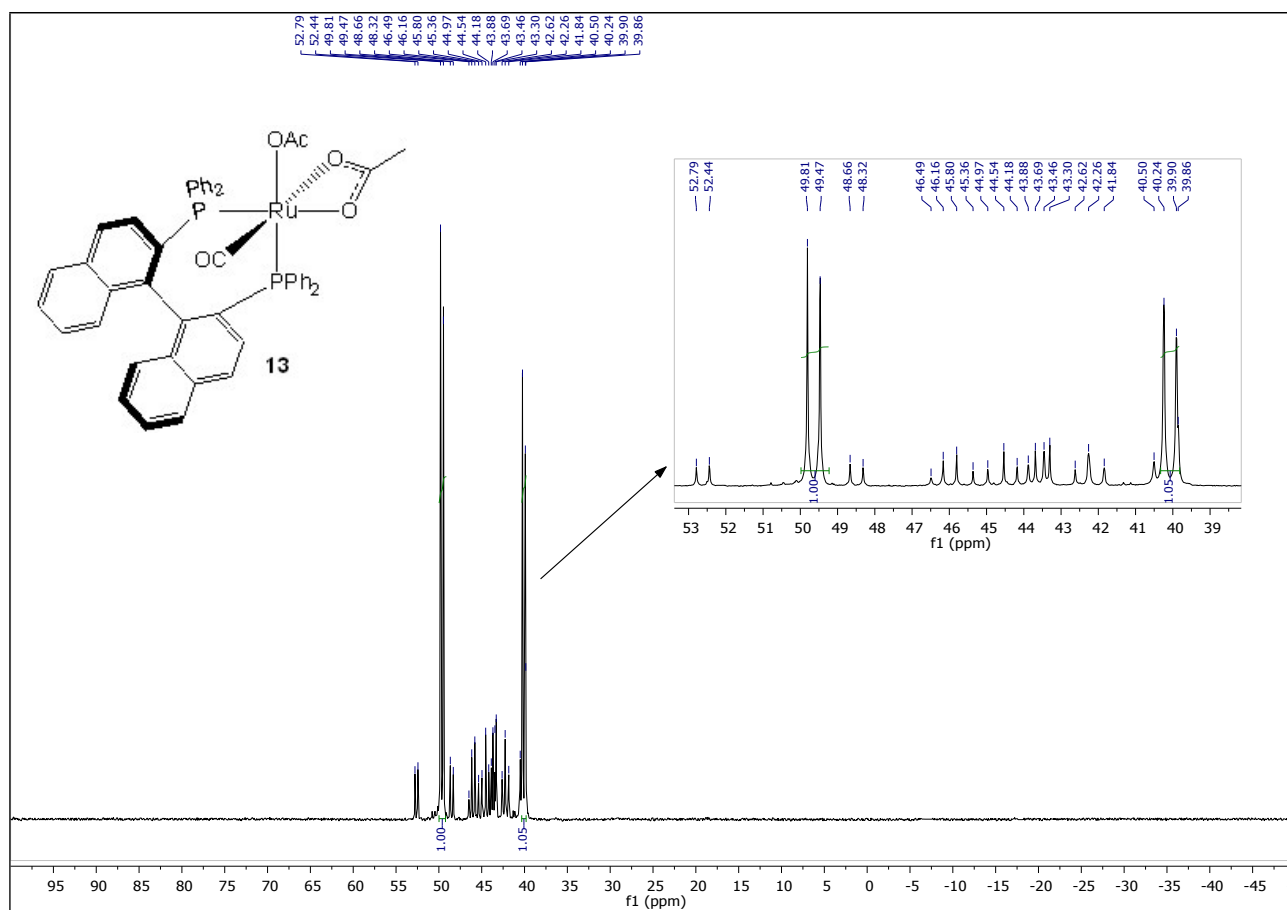
**Figure S48.** <sup>13</sup>C{<sup>1</sup>H} PENDANT NMR spectrum (50.3 MHz) of [Ru(OAc)<sub>2</sub>(CO)(dppf)] (**12**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.



**Figure S49.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})(\text{dppf})]$  (**12**) in  $\text{CD}_2\text{Cl}_2$  at  $-70\text{ }^\circ\text{C}$ .

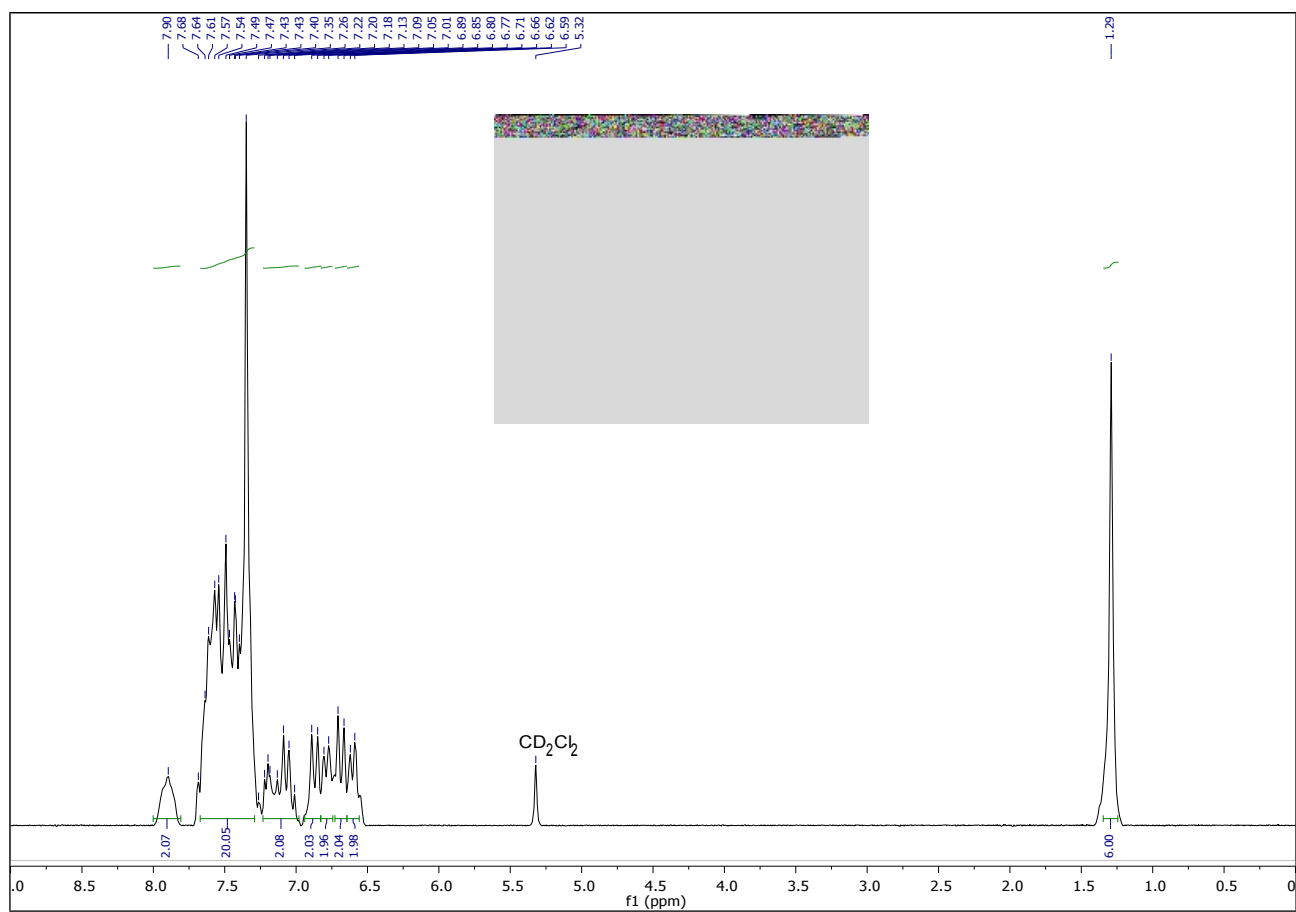


**Figure S50.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})((R)\text{-BINAP})]$  (**13**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.

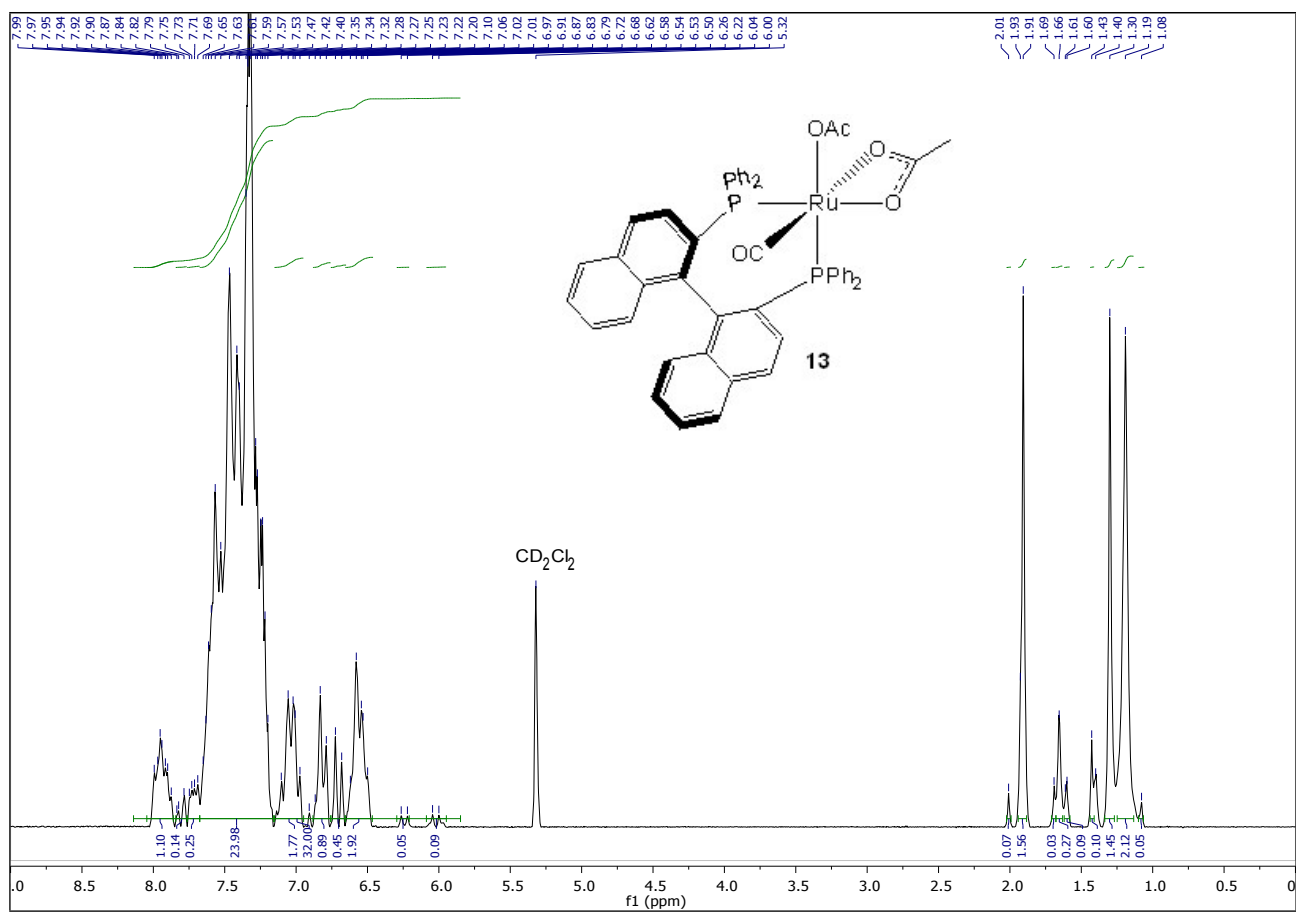


**Figure S51.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})((R)\text{-BINAP})]$  (**13**) in  $\text{CD}_2\text{Cl}_2$  at  $-60\text{ }^\circ\text{C}$ .

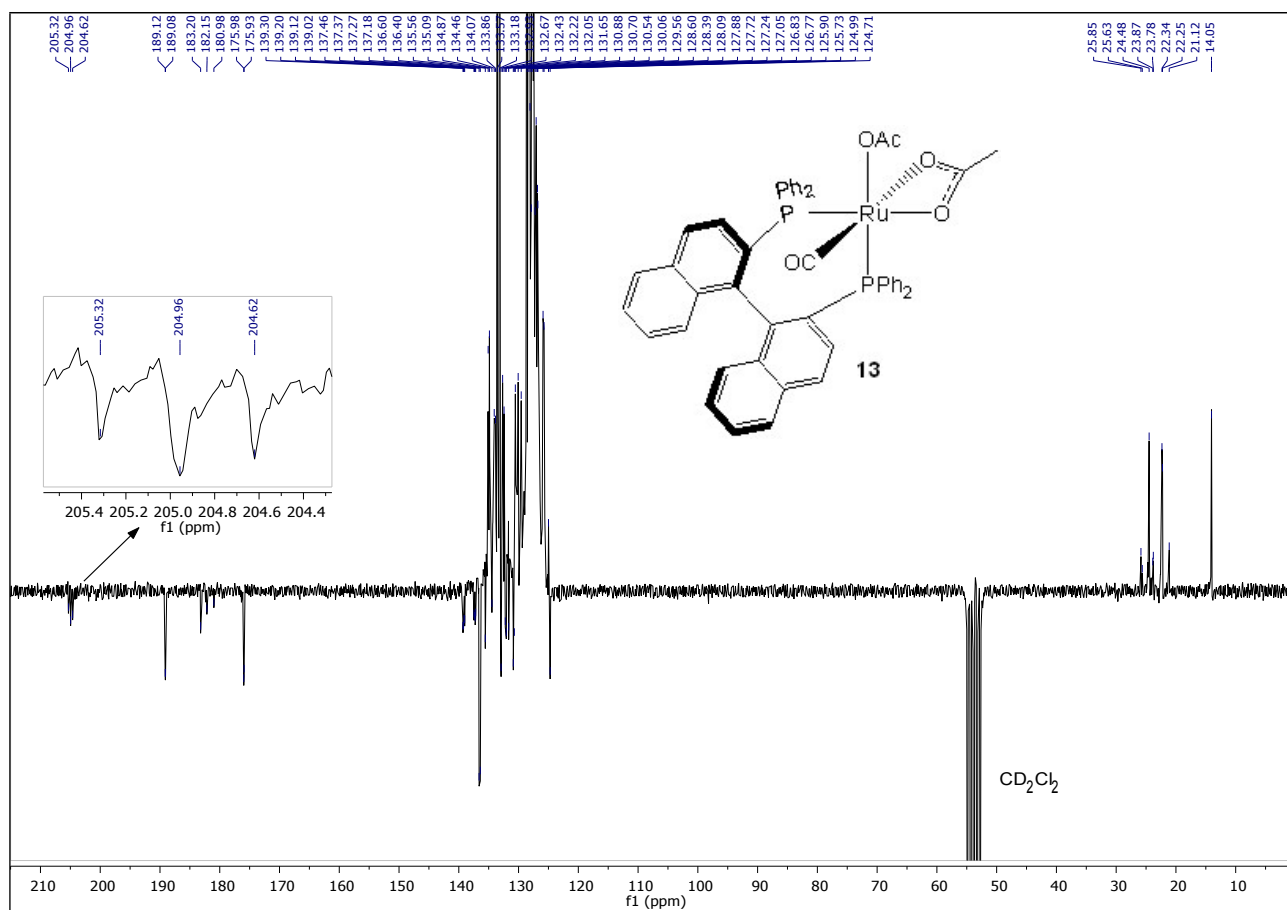




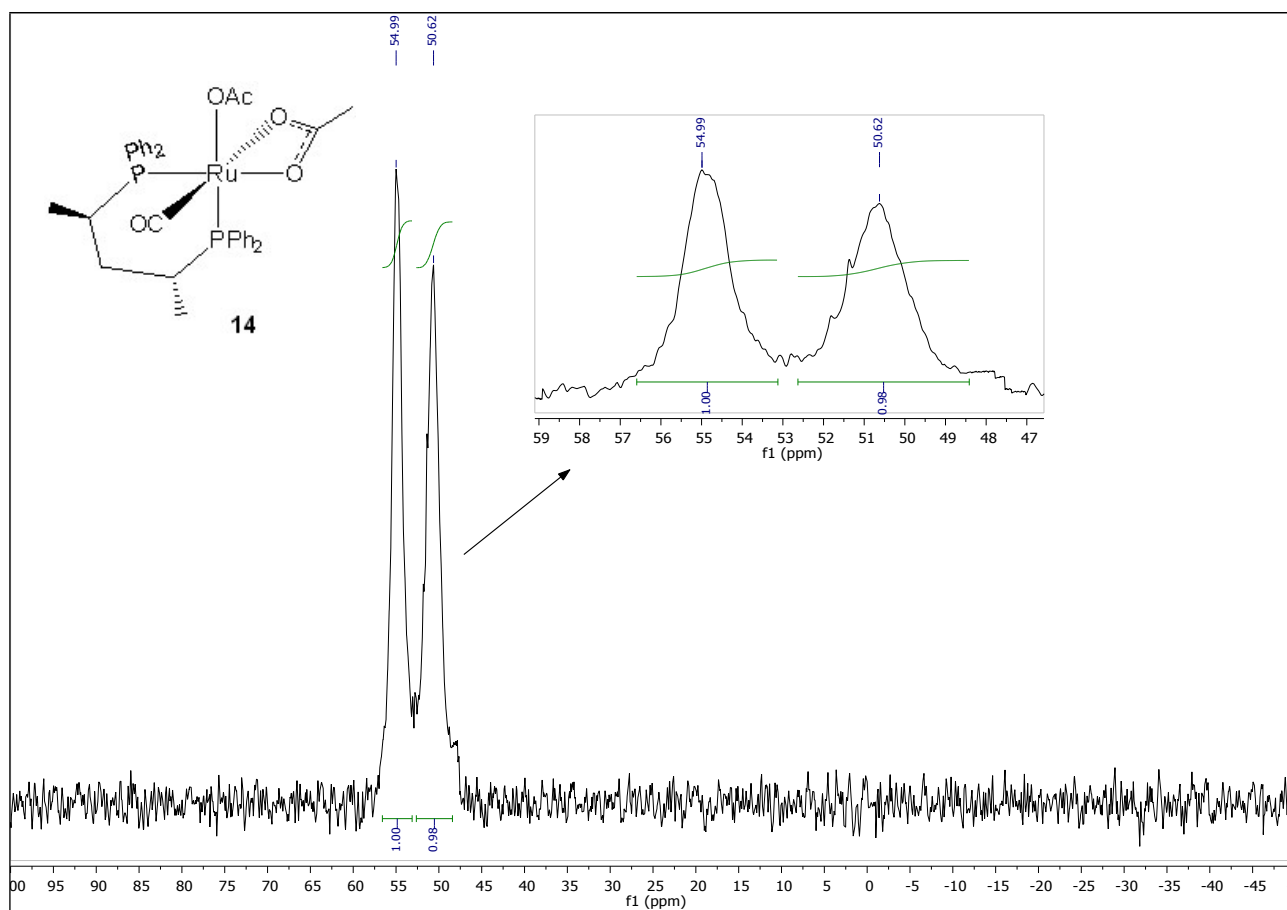
**Figure S52.**  $^1\text{H}$  NMR spectrum (200.1 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})((R)\text{-BINAP})]$  (**13**) in  $\text{CD}_2\text{Cl}_2$  at 20  $^\circ\text{C}$ .



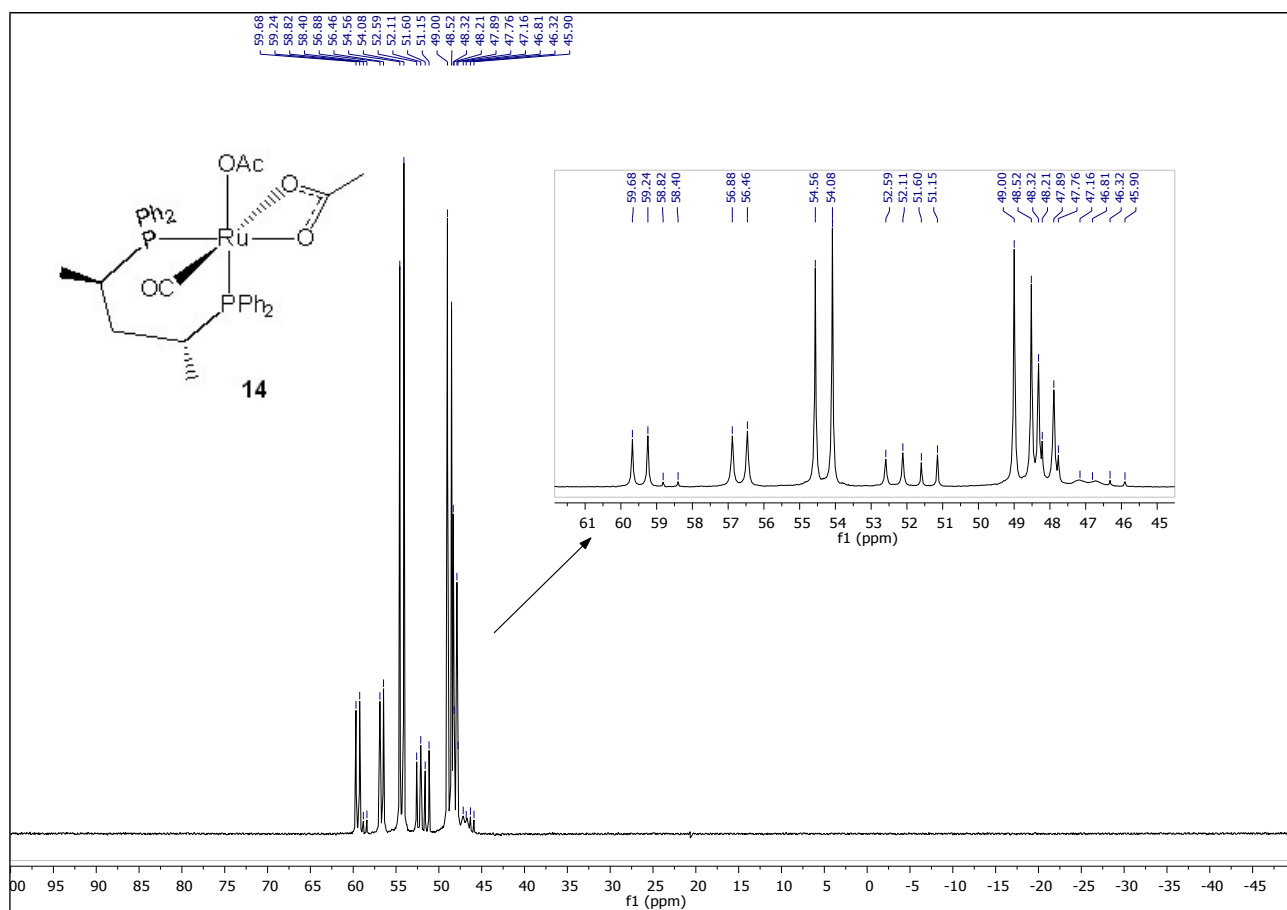
**Figure S53.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [Ru(OAc)<sub>2</sub>(CO)((*R*)-BINAP)] (**13**) in CD<sub>2</sub>Cl<sub>2</sub> at -60 °C.



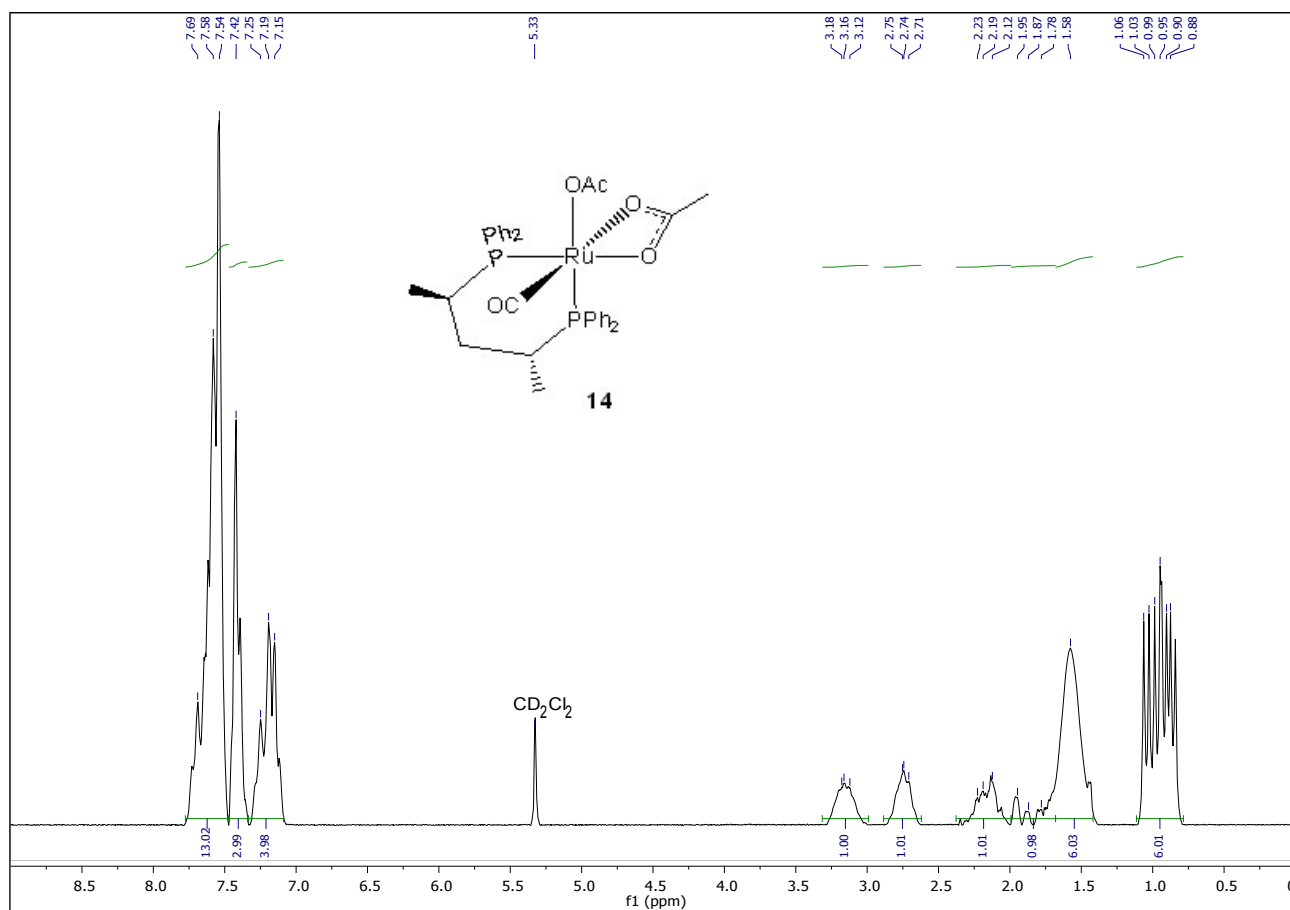
**Figure S54.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})((R)\text{-BINAP})]$  (**13**) in  $\text{CD}_2\text{Cl}_2$  at  $-60\text{ }^\circ\text{C}$ .



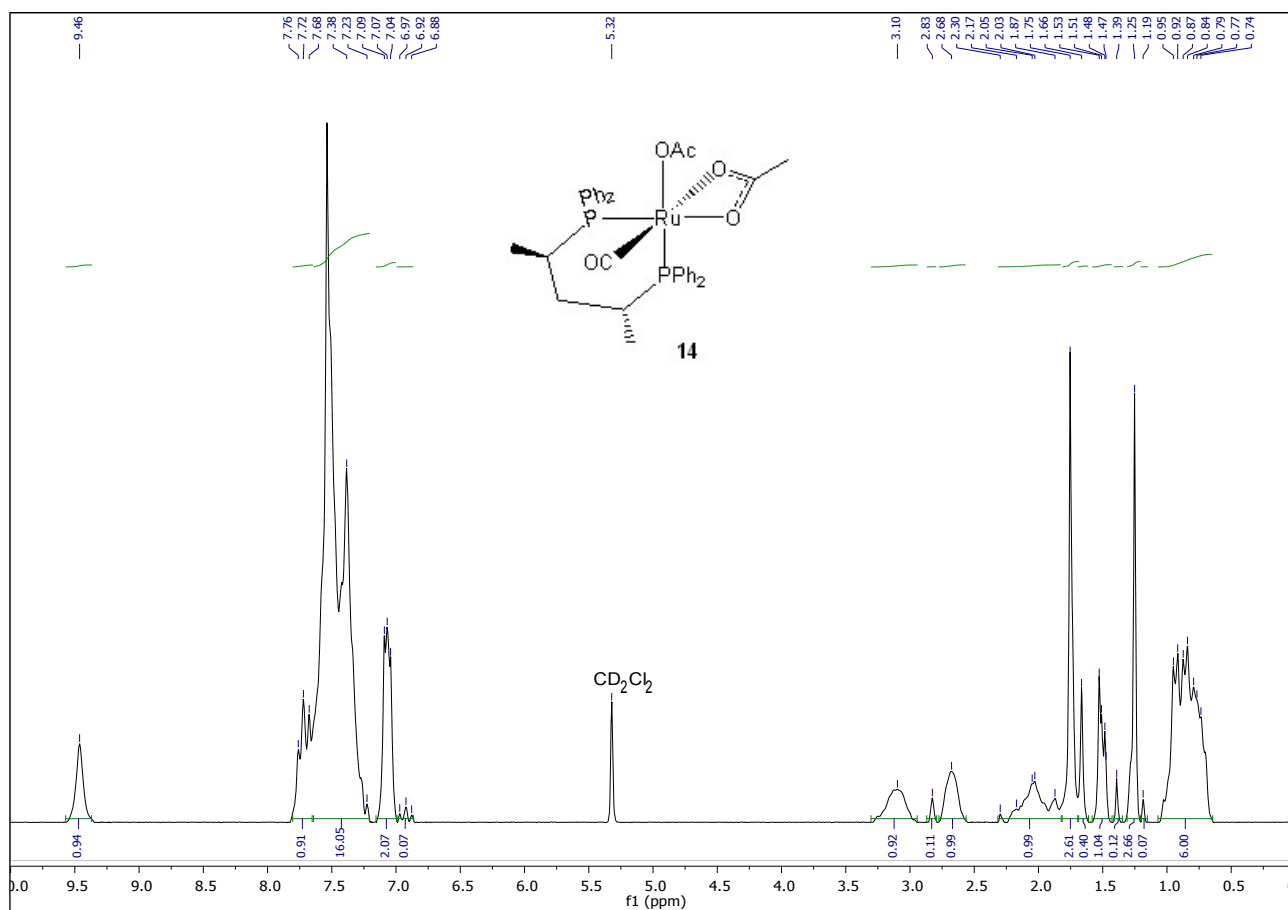
**Figure S55.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})((R,R)\text{-Skewphos})]$  (**14**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.



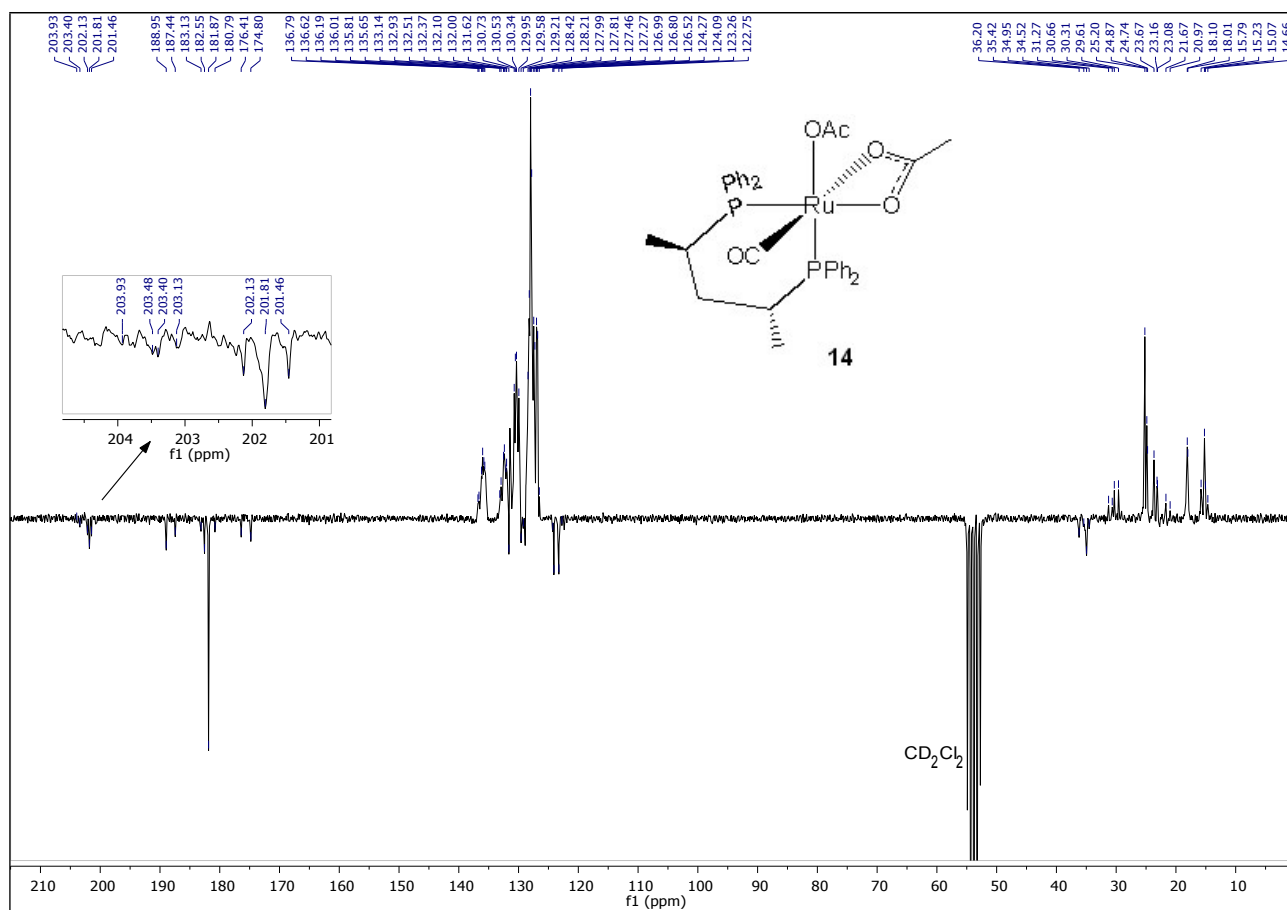
**Figure S56.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})((R,R)\text{-Skewphos})]$  (**14**) in  $\text{CD}_2\text{Cl}_2$  at  $-60\text{ }^\circ\text{C}$ .



**Figure S57.**  $^1\text{H}$  NMR spectrum (200.1 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})((R,R)\text{-Skewphos})]$  (**14**) in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$ .

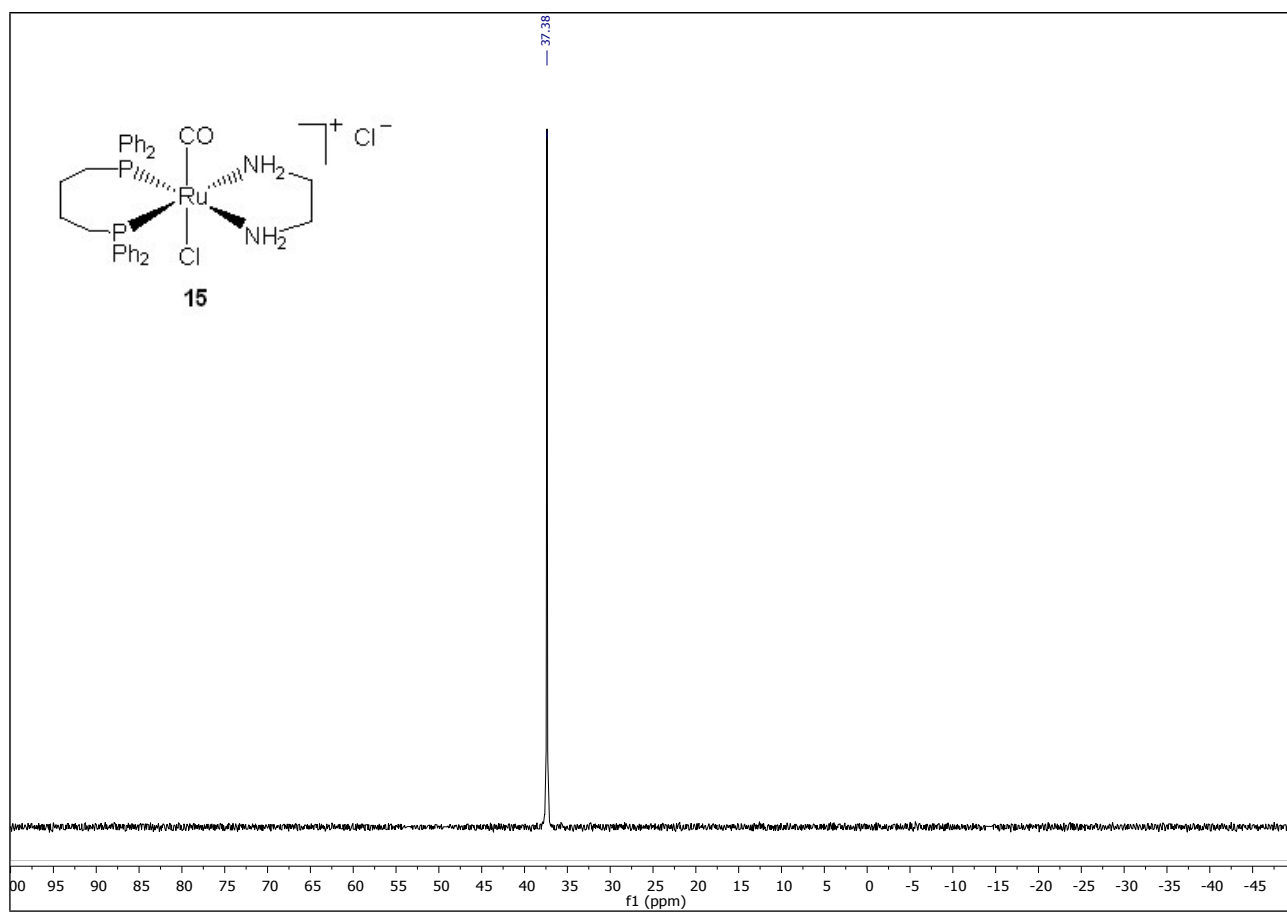


**Figure S58.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [Ru(OAc)<sub>2</sub>(CO)((*R,R*)-Skewphos)] (**14**) in CD<sub>2</sub>Cl<sub>2</sub> at -60 °C.

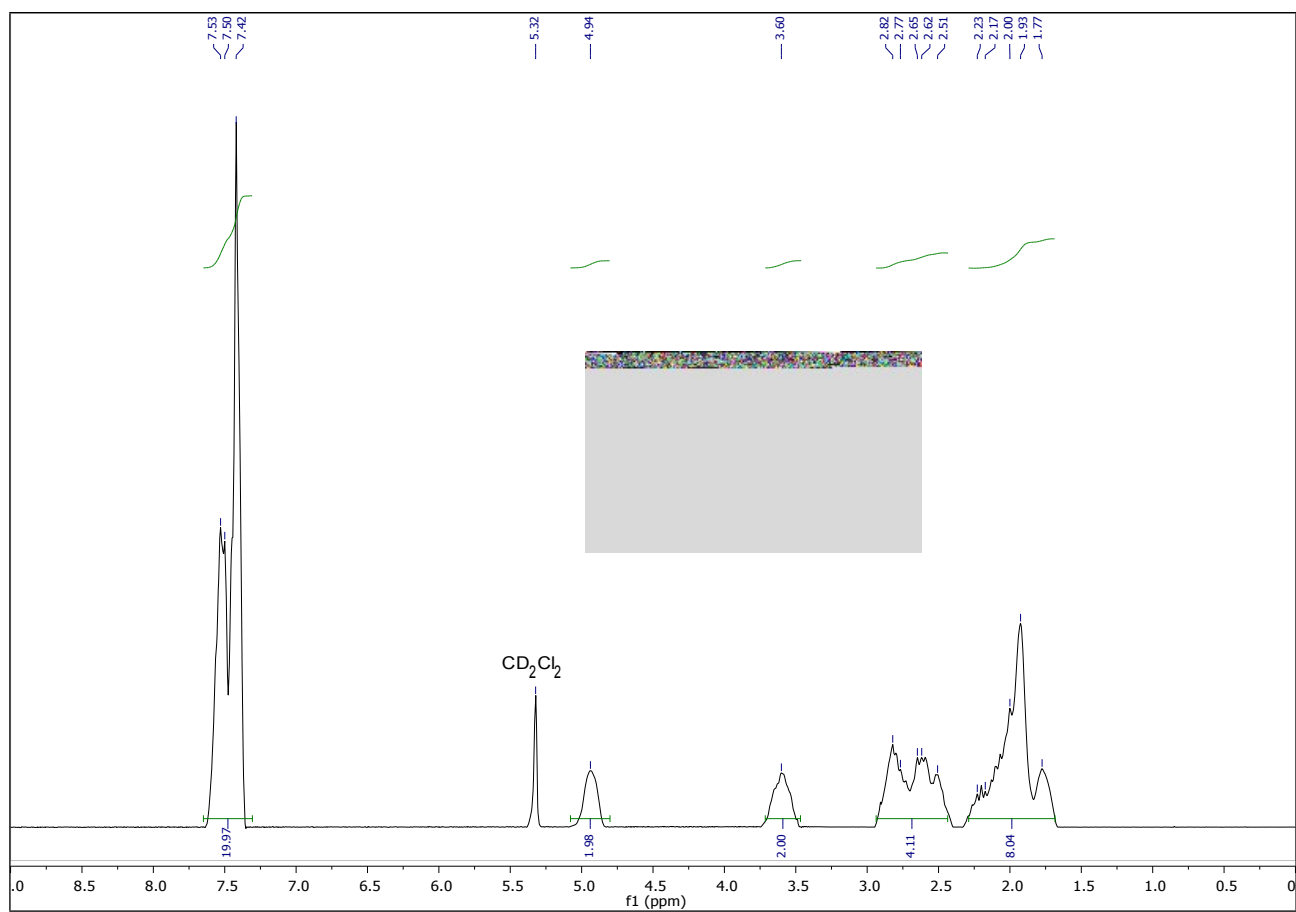


**Figure S59.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})_2(\text{CO})((R,R)\text{-Skewphos})]$  (**14**) in  $\text{CD}_2\text{Cl}_2$  at  $-60\text{ }^\circ\text{C}$ .

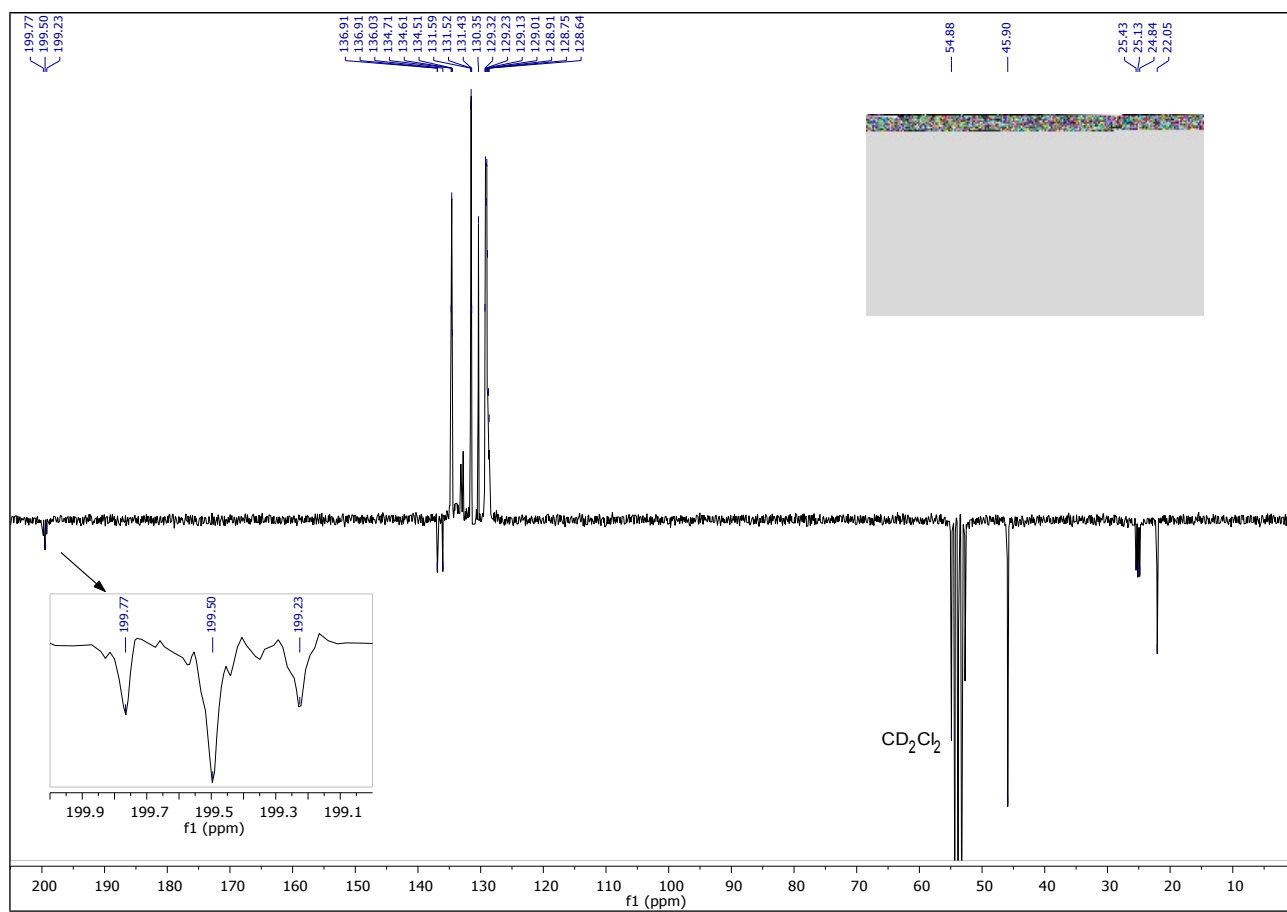




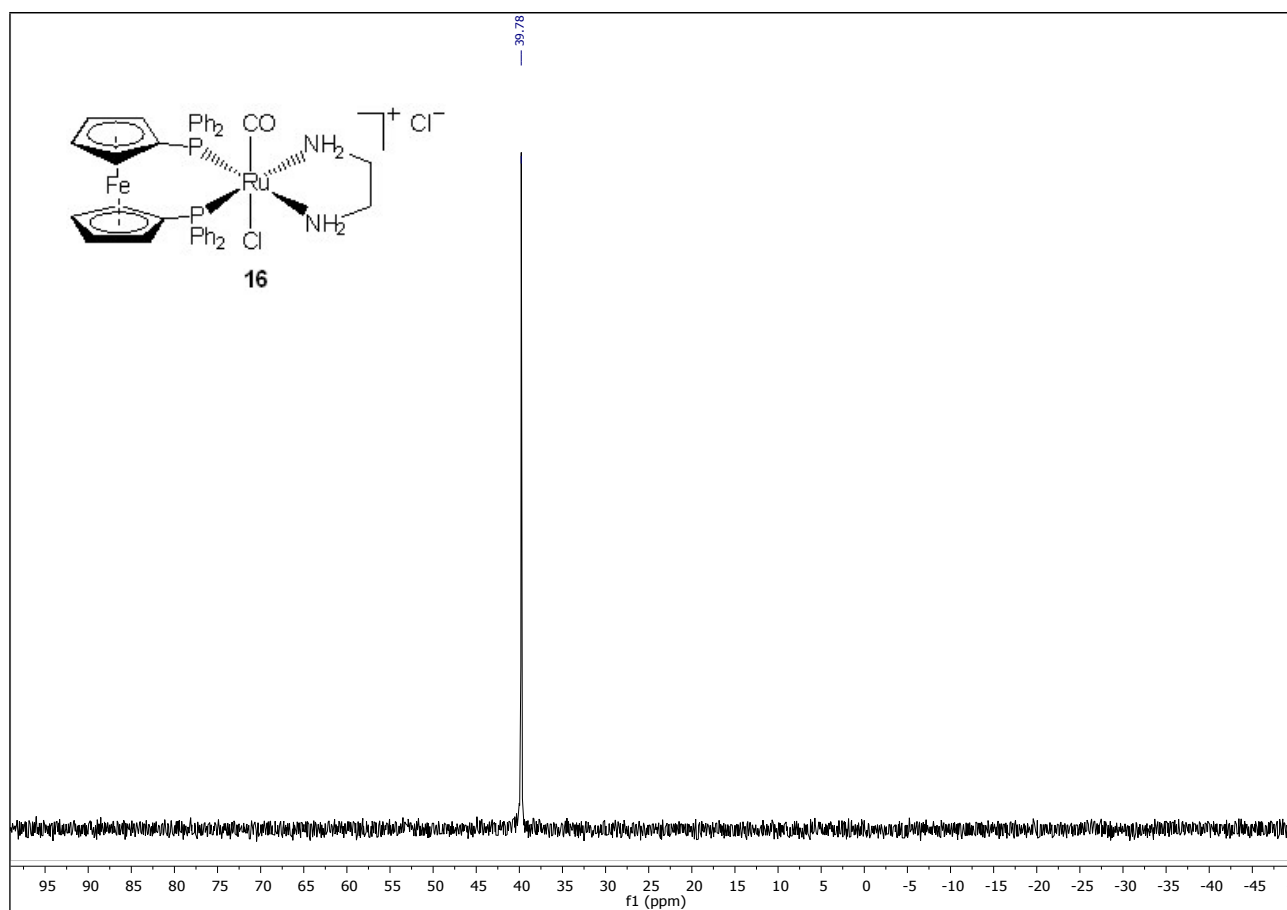
**Figure S60.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{RuCl}(\text{CO})(\text{dppb})(\text{en})]\text{Cl}$  (**15**) in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$ .



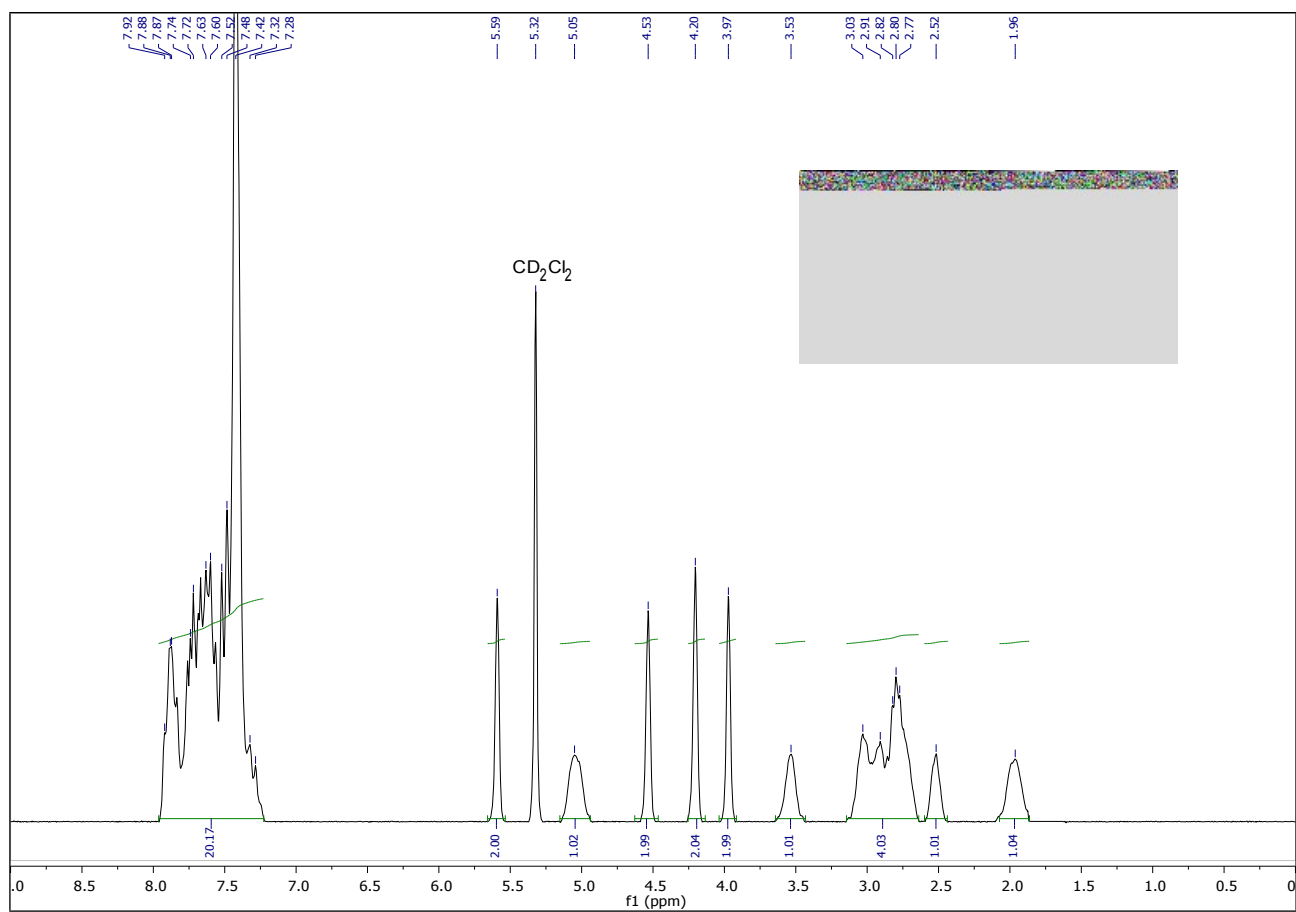
**Figure S61.**  $^1\text{H}$  NMR spectrum (200.1 MHz) of  $[\text{RuCl}(\text{CO})(\text{dppb})(\text{en})]\text{Cl}$  (**15**) in  $\text{CD}_2\text{Cl}_2$  at  $20\text{ }^\circ\text{C}$ .



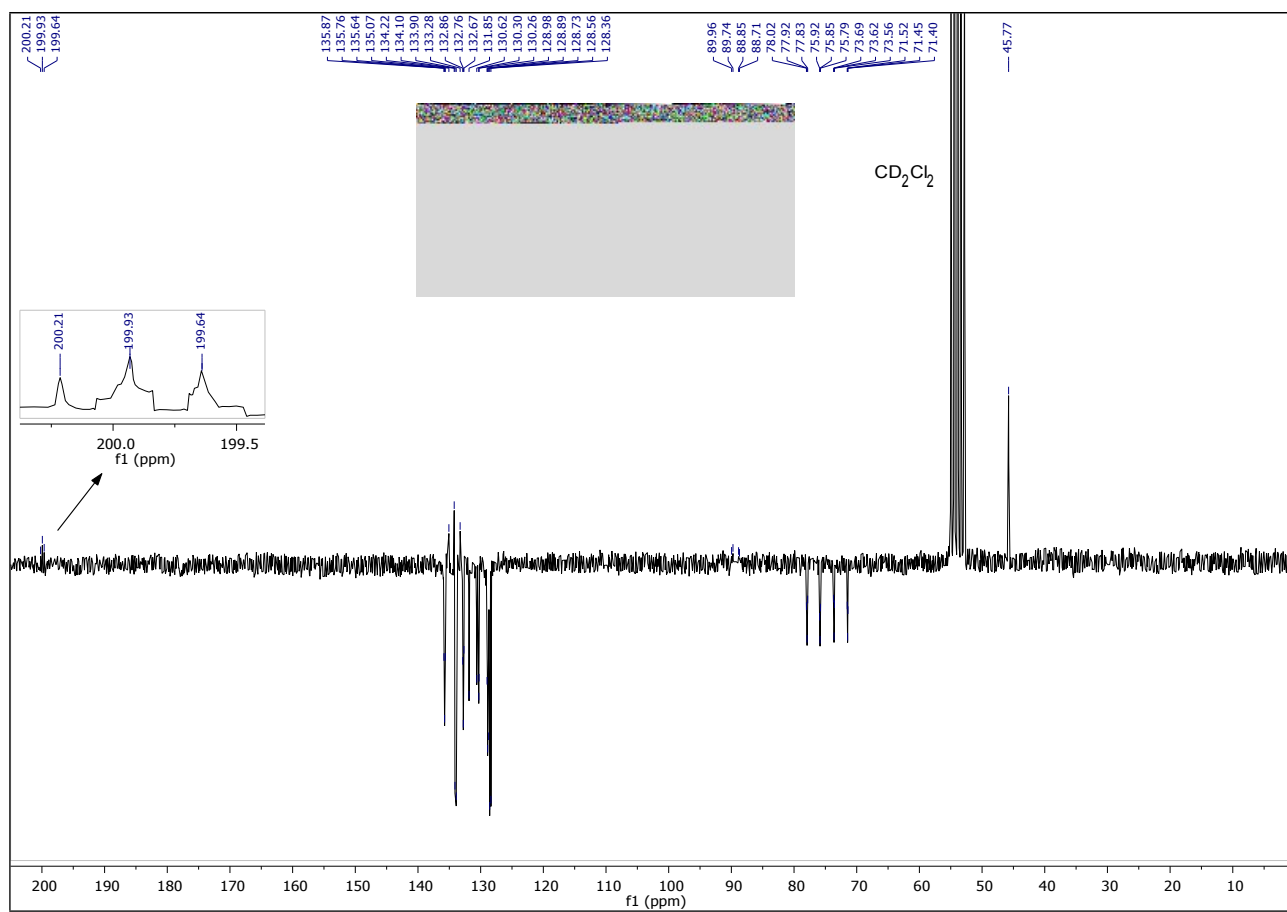
**Figure S62.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{RuCl}(\text{CO})(\text{dppb})(\text{en})]\text{Cl}$  (**15**) in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$



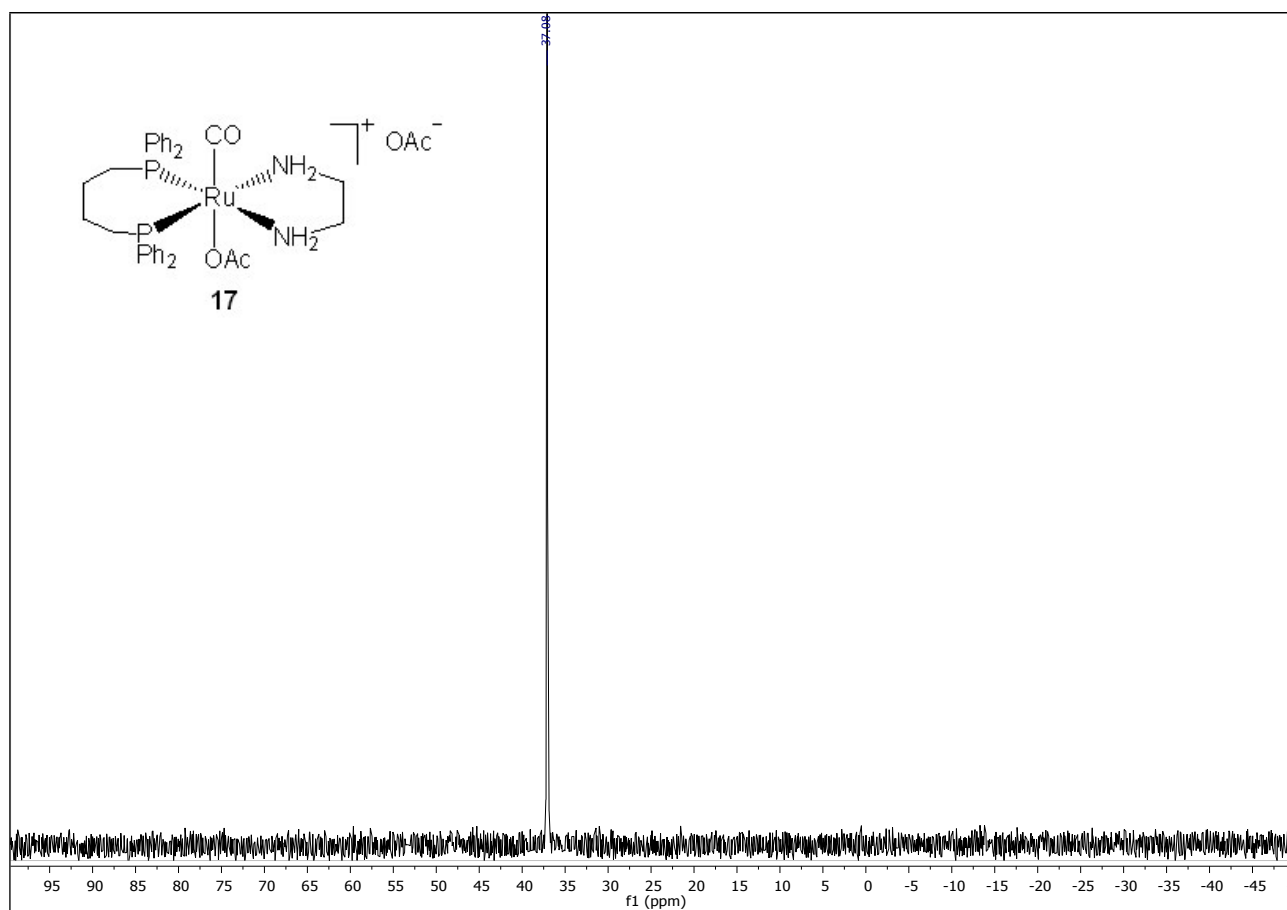
**Figure S63.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{RuCl}(\text{CO})(\text{dppf})(\text{en})]\text{Cl}$  (**16**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.



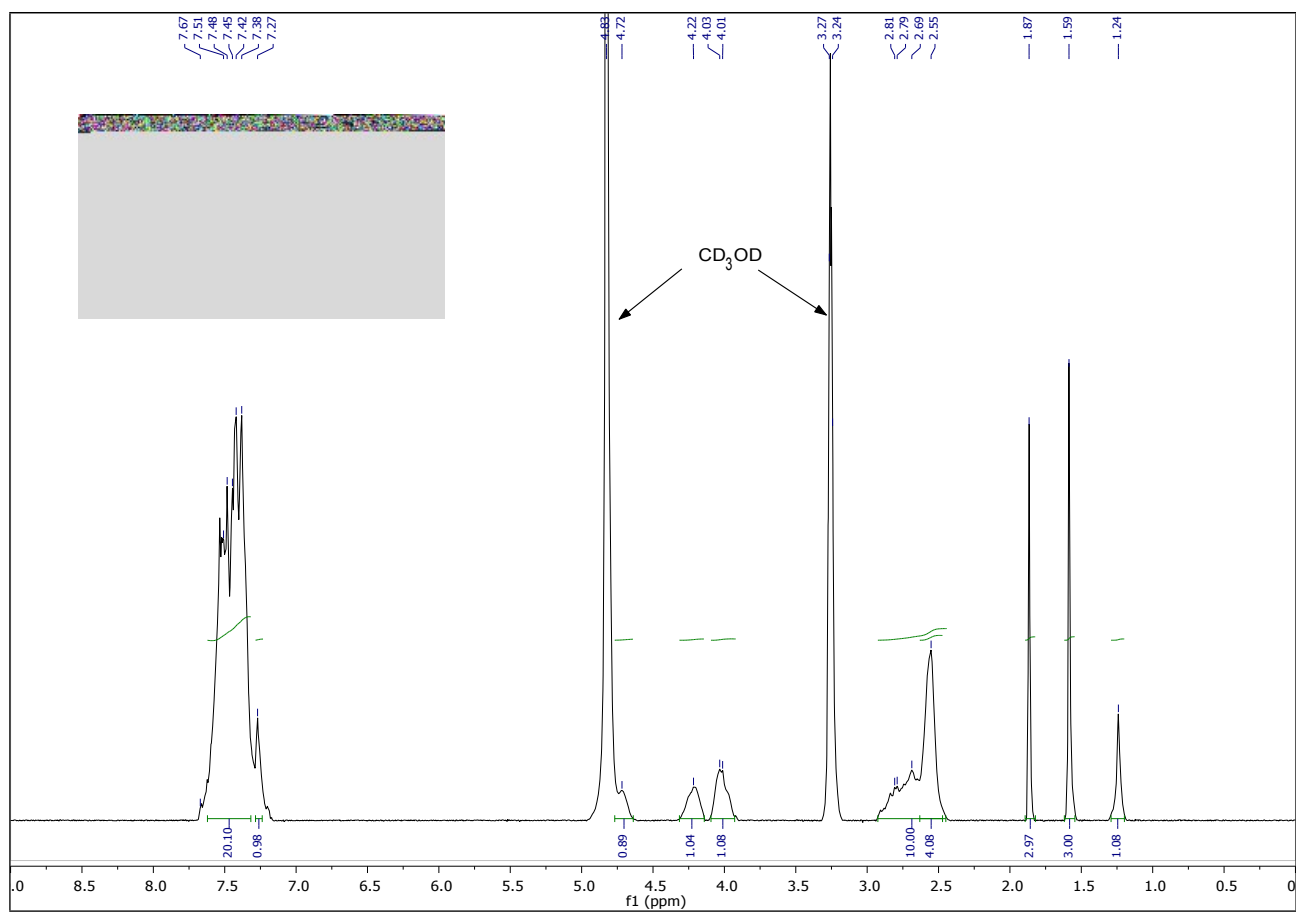
**Figure S64.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [RuCl(CO)(dppf)(en)]Cl (**16**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.



**Figure S65.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{RuCl}(\text{CO})(\text{dppf})(\text{en})]\text{Cl}$  (16) in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$ .

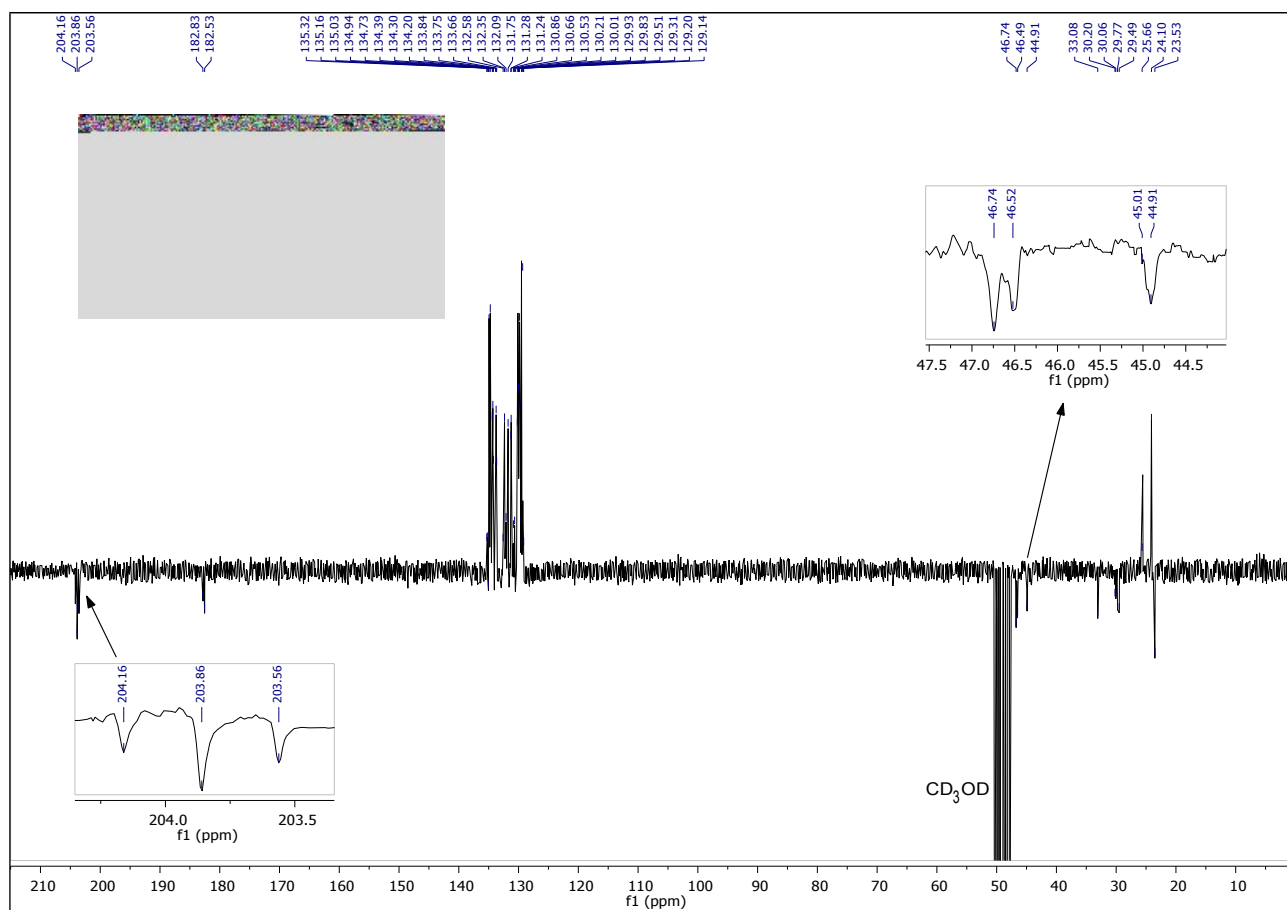


**Figure S66.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppb})(\text{en})]\text{OAc}$  (**17**) in  $\text{CD}_3\text{OD}$  at  $20^\circ\text{C}$ .

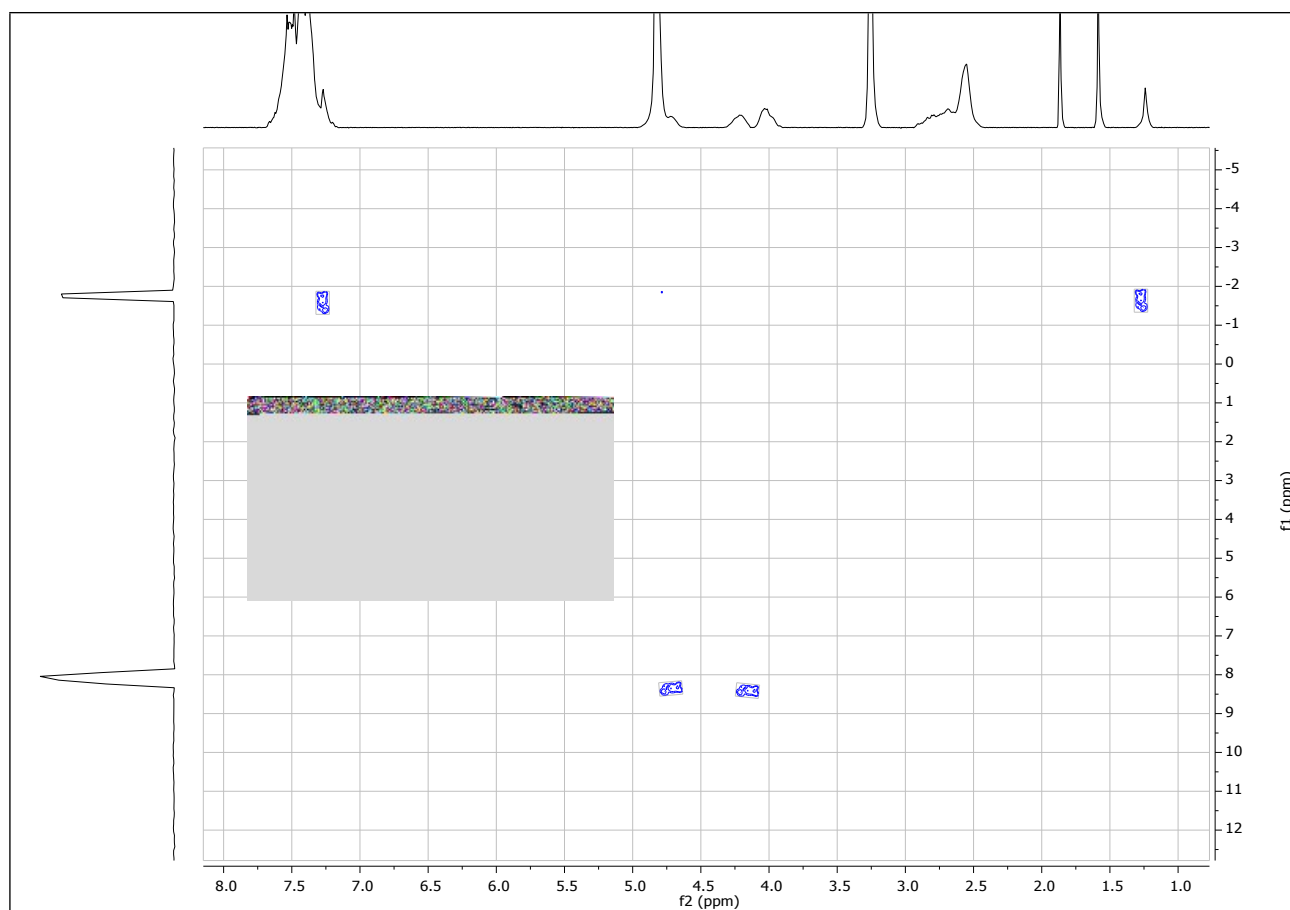


**Figure S67.**  $^1\text{H}$  NMR spectrum (200.1 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppb})(\text{en})]\text{OAc}$  (**17**) in  $\text{CD}_3\text{OD}$  at  $20\text{ }^\circ\text{C}$ .

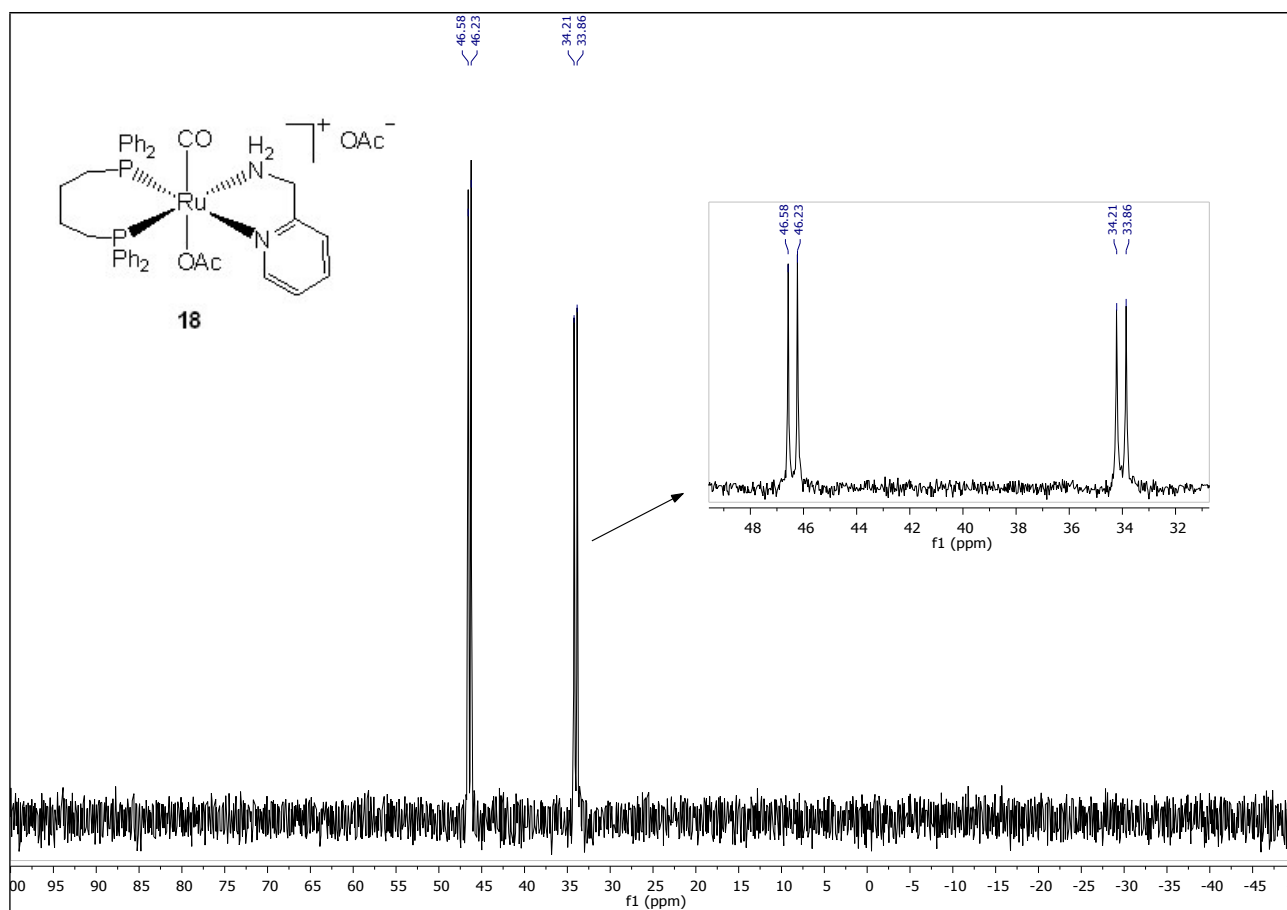




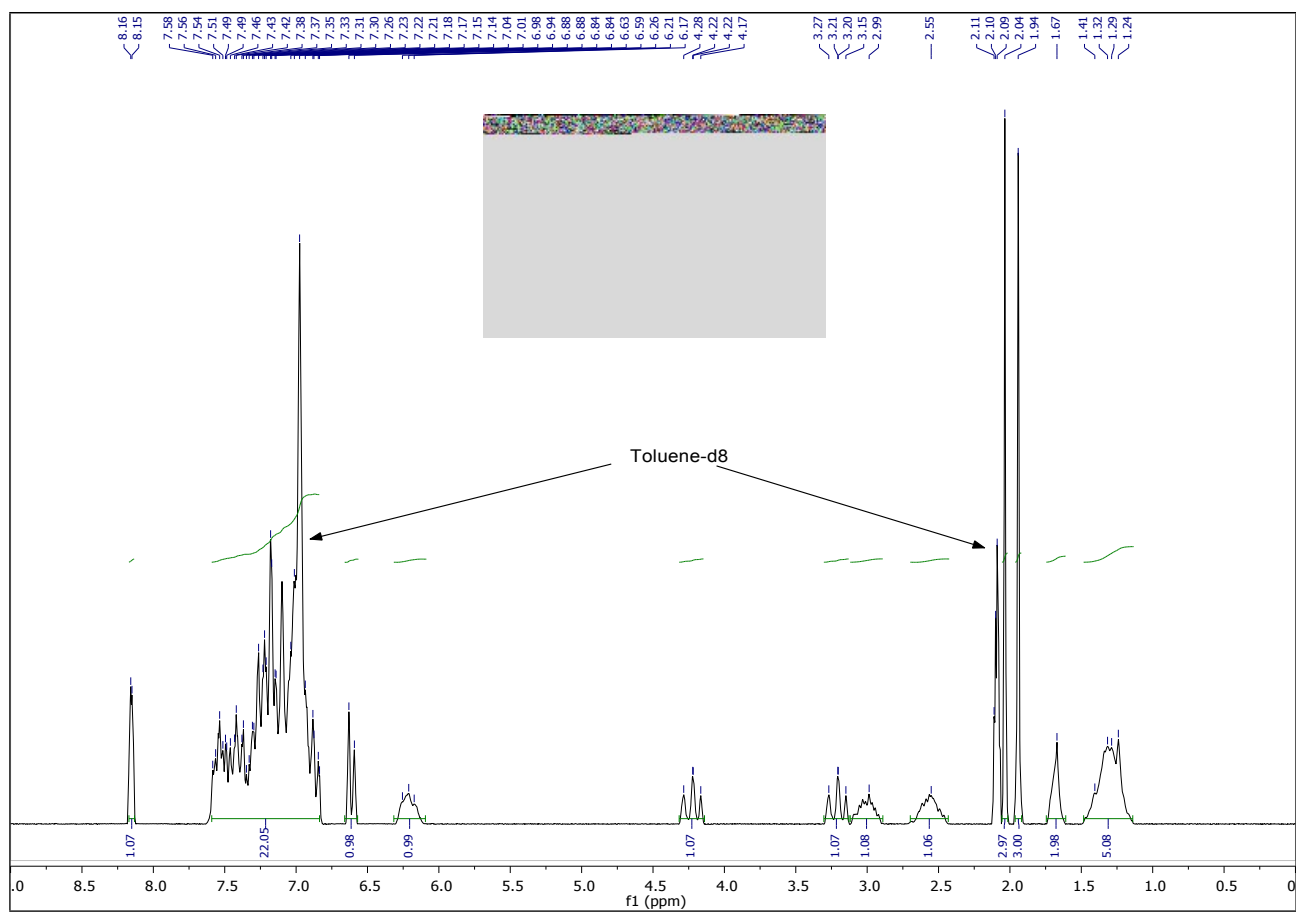
**Figure S68.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppb})(\text{en})]\text{OAc}$  (17) in  $\text{CD}_3\text{OD}$  at  $20^\circ\text{C}$ .



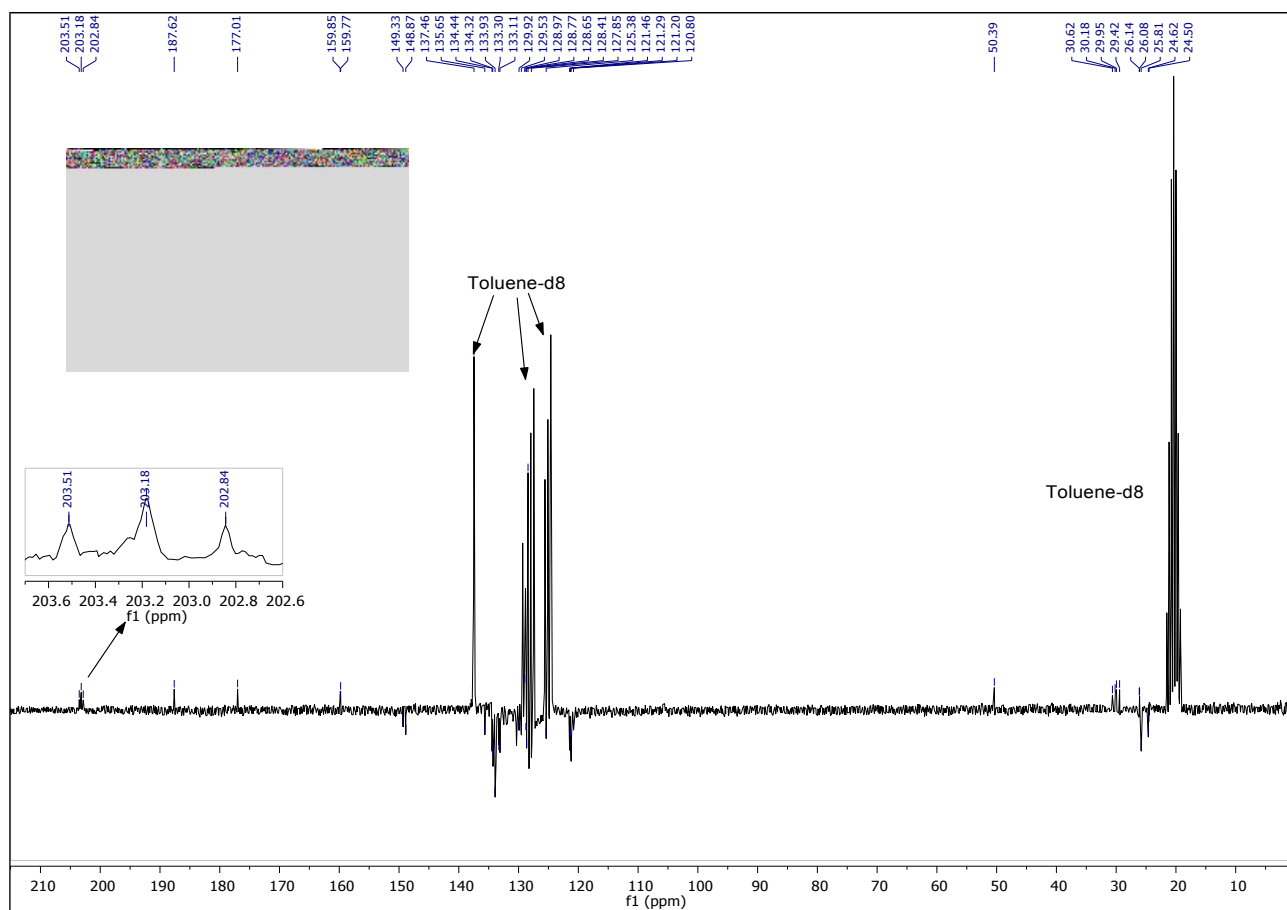
**Figure S69.**  $^{15}\text{N}$ - $^1\text{H}$  HSQC 2D NMR spectrum of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppb})(\text{en})]\text{OAc}$  (**17**) in  $\text{CD}_3\text{OD}$  at  $20\text{ }^\circ\text{C}$ .



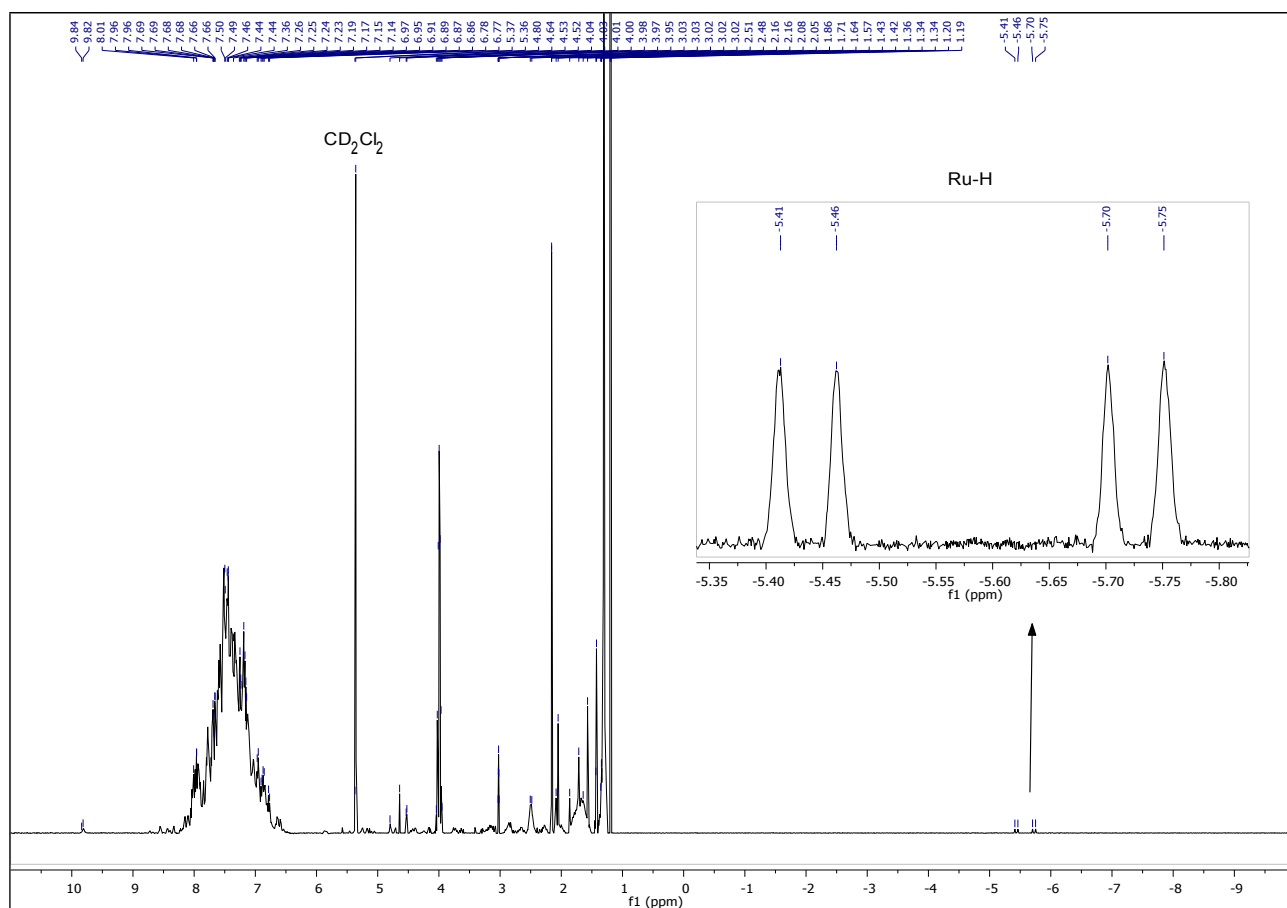
**Figure S70.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppb})(\text{ampy})]\text{OAc}$  (**18**) in  $[\text{D}_8]\text{toluene}$  at  $20\text{ }^\circ\text{C}$ .



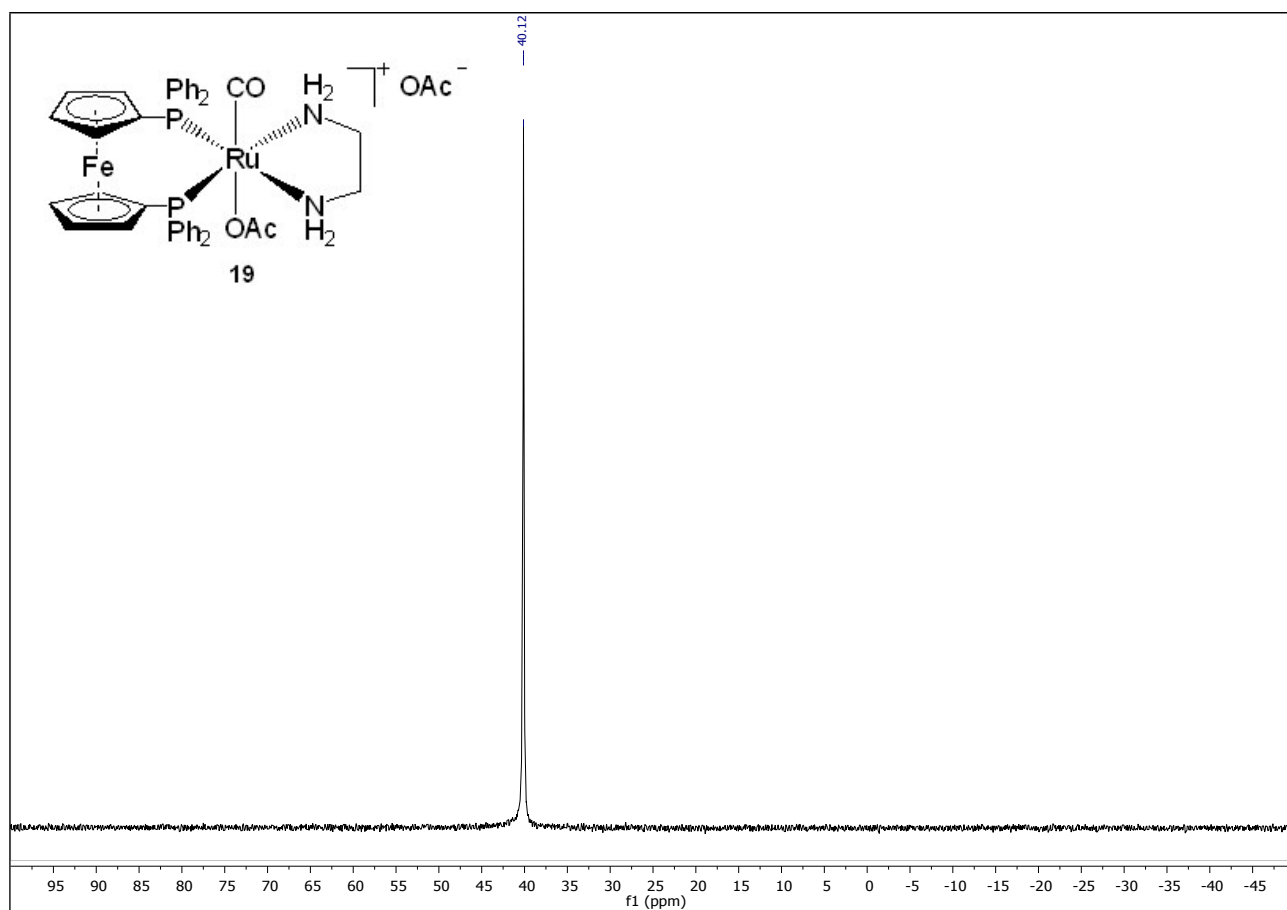
**Figure S71.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [Ru(OAc)(CO)(dppb)(ampy)]OAc (**18**) in [D8]toluene at 20 °C.



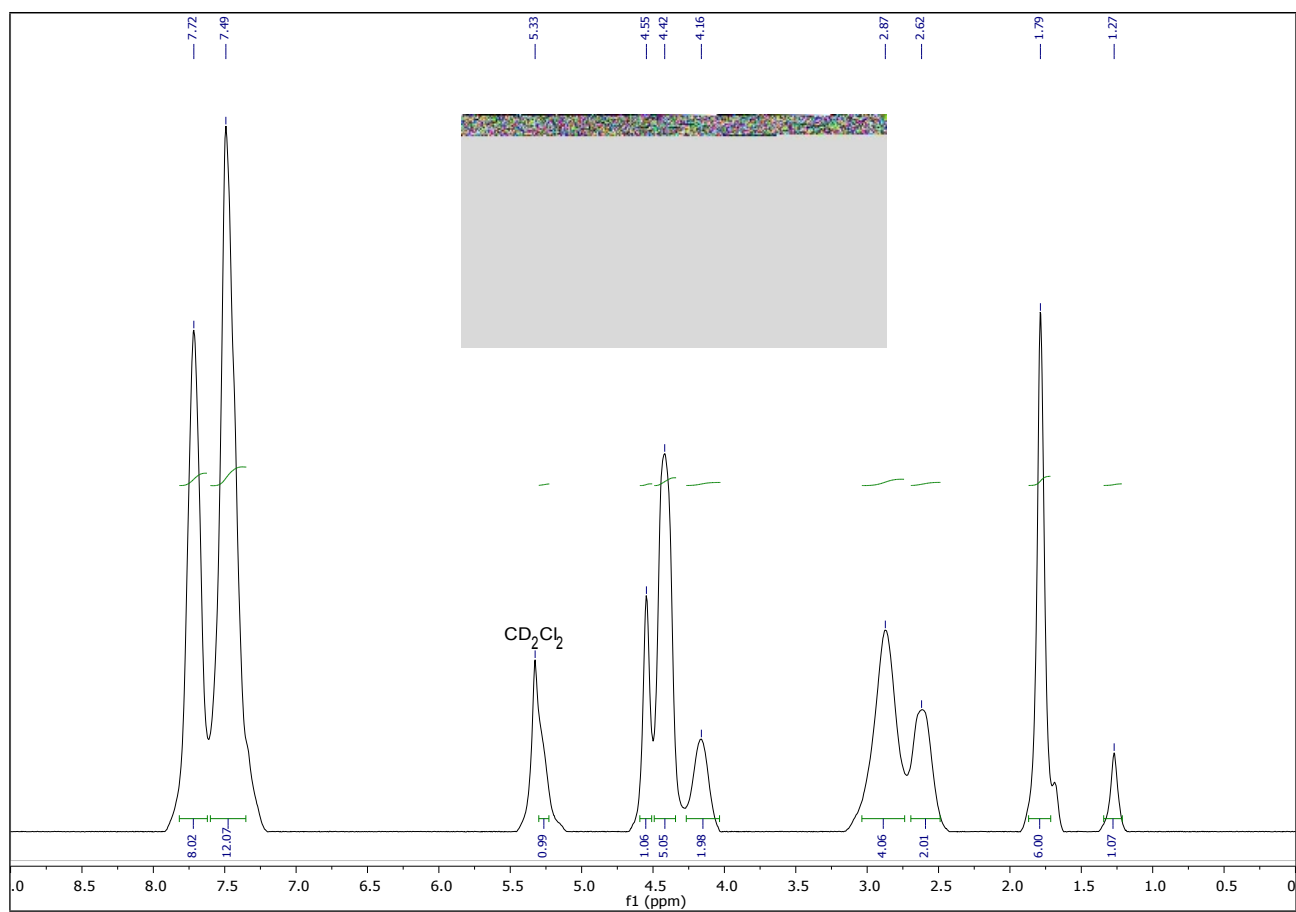
**Figure S72.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppb})(\text{ampy})]\text{OAc}$  (**18**) in  $[\text{D}_8]\text{toluene}$  at  $20\text{ }^\circ\text{C}$ .



**Figure S73.**  $^1\text{H}$  NMR spectrum (400.1 MHz,  $\text{CD}_2\text{Cl}_2$ , 20 °C) which evidences of the formation of a ruthenium monohydride species from  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppb})(\text{ampy})]\text{OAc}$  (**18**), by treatment with 2 eq. of  $\text{NaOiPr}$  in 2-propanol.

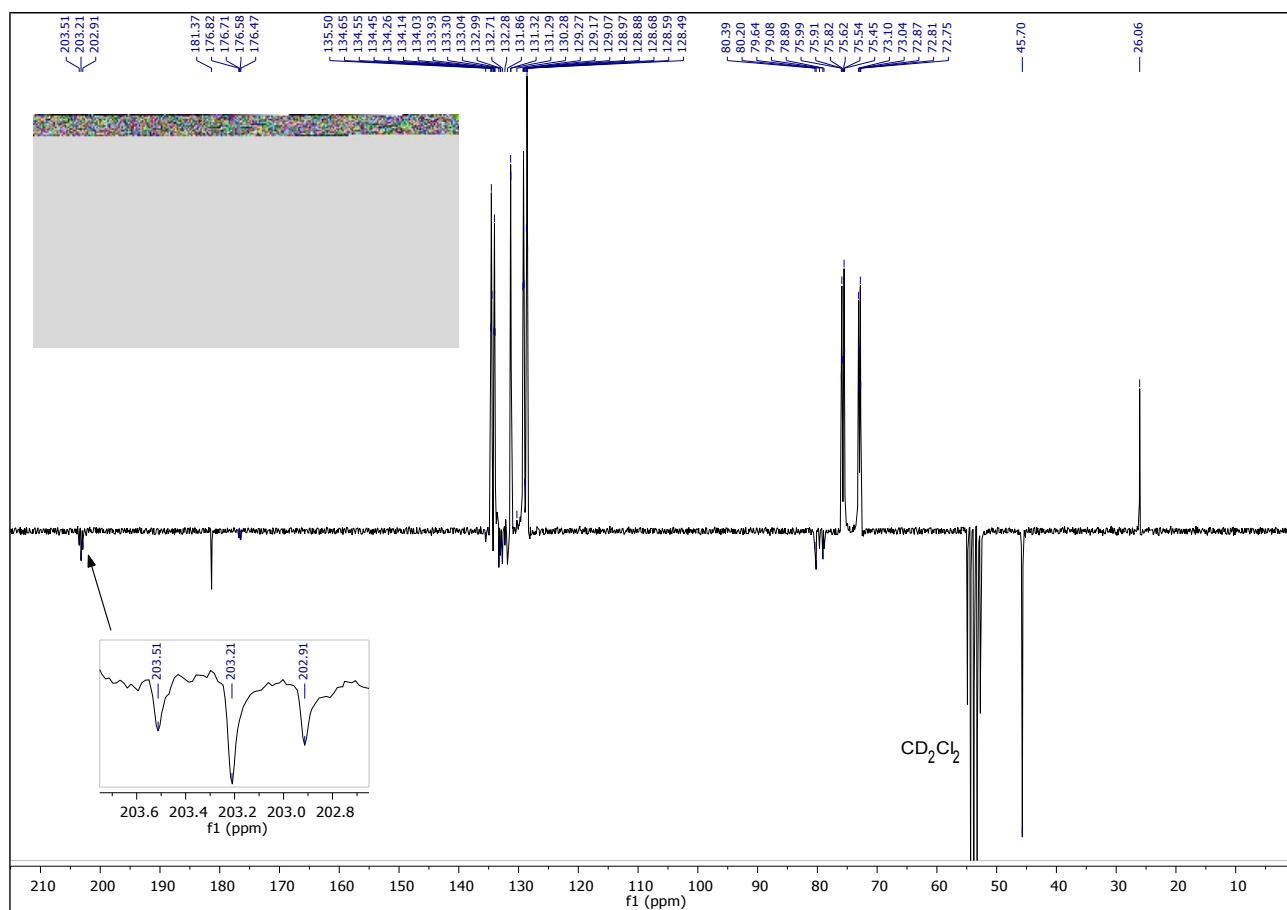


**Figure S74.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppf})(\text{en})]\text{OAc}$  (**19**) in  $\text{CD}_2\text{Cl}_2$  at 20 °C.

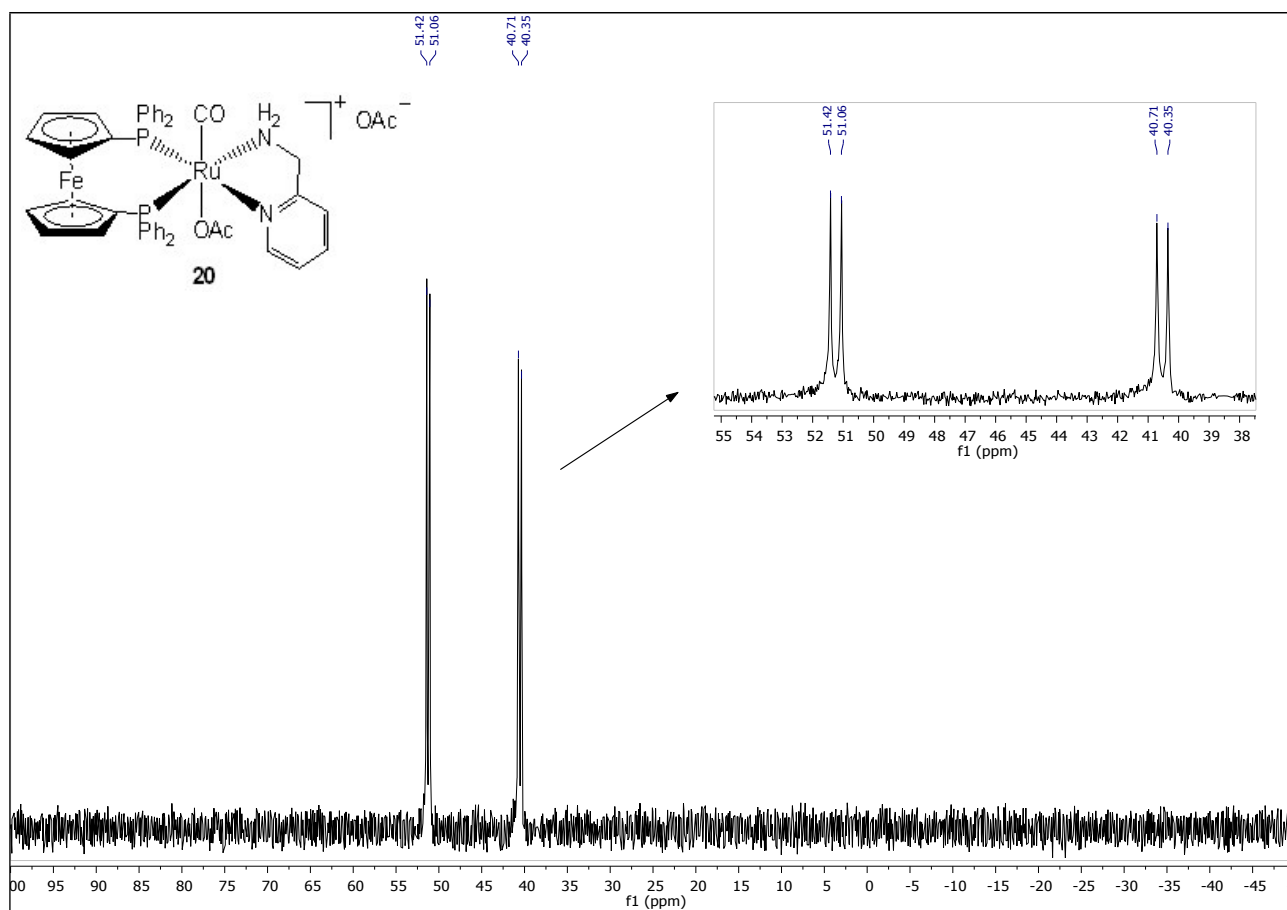


**Figure S75.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [Ru(OAc)(CO)(dppf)(en)]OAc (**19**) in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C.

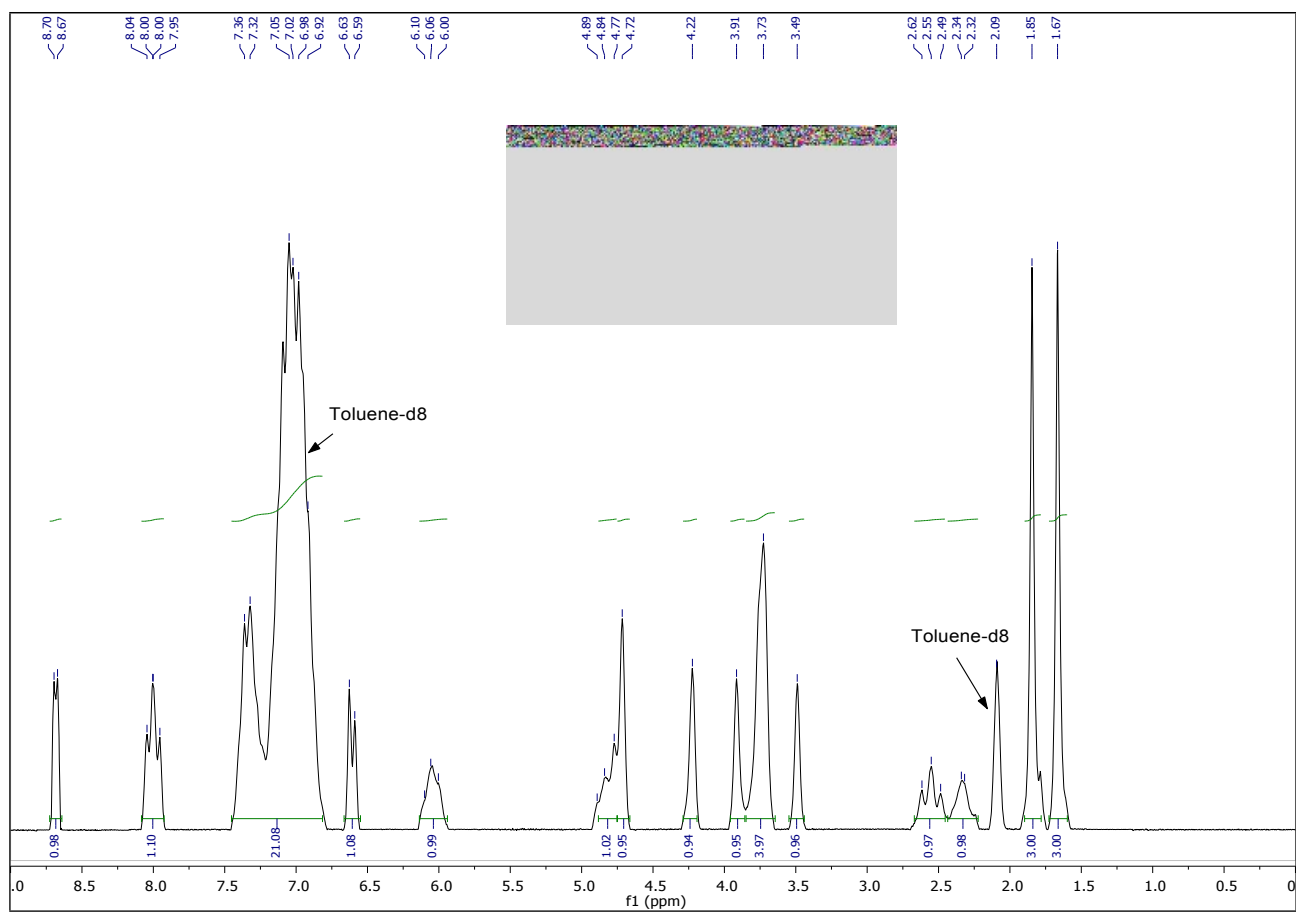




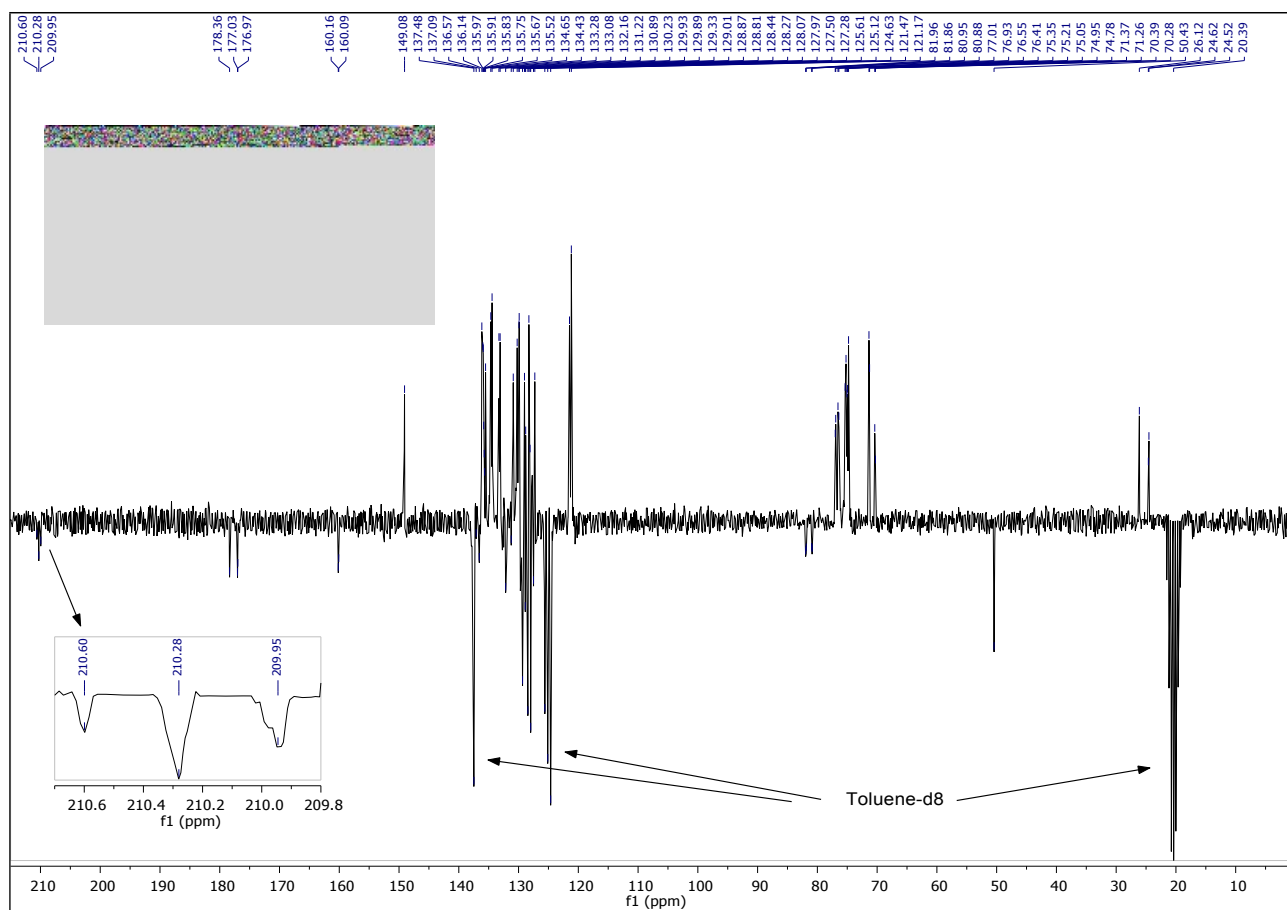
**Figure S76.**  $^{13}\text{C}\{^1\text{H}\}$  PENDANT NMR spectrum (50.3 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppf})(\text{en})]\text{OAc}$  (**19**) in  $\text{CD}_2\text{Cl}_2$  at  $20\text{ }^\circ\text{C}$ .



**Figure S77.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppf})(\text{ampy})]\text{OAc}$  (**20**) in  $[\text{D}_8]\text{toluene}$  at 20 °C.



**Figure S78.** <sup>1</sup>H NMR spectrum (200.1 MHz) of [Ru(OAc)(CO)(dppf)(ampy)]OAc (**20**) in [D<sub>8</sub>]toluene at 20 °C.



**Figure S79.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (81.0 MHz) of  $[\text{Ru}(\text{OAc})(\text{CO})(\text{dppf})(\text{ampy})]\text{OAc}$  (**20**) in  $[\text{D}_8]\text{toluene}$  at  $20\text{ }^\circ\text{C}$ .

**Table S1.** Further data regarding the catalytic TH of acetophenone (0.1 M) with complexes **6-14** (S/C 1000) in 2-propanol at 82 °C, and in the presence of NaOiPr 2 mol%.

Entry	Complex	Ligand (5 equiv.)	Time [min]	Conv. <sup>[a]</sup> [%]	TOF <sup>[b]</sup> [h <sup>-1</sup> ]	e.e. (%)
1	<b>6</b>	en	120	25	-	-
2	<b>7</b>	en	120	44	-	-
3	<b>8</b>	en	120	92	900	22 ( <i>S</i> )
4	<b>8</b>	ampy	300	88	300	18 ( <i>S</i> )
5	<b>8</b>	(±)- <i>i</i> Pr-ampy <sup>[c]</sup>	120	97	1200	25 ( <i>S</i> )
6	<b>8</b>	( <i>S,S</i> )-DPEN	120	78	1100	16 ( <i>S</i> )
7	<b>9</b>	en	120	74	400	13 ( <i>S</i> )
8	<b>9</b>	ampy	120	95	1700	17 ( <i>R</i> )
9	<b>9</b>	(±)- <i>i</i> Pr-ampy <sup>[c]</sup>	30	97	6700	17 ( <i>R</i> )
10	<b>9</b>	( <i>S,S</i> )-DPEN	120	94	700	32 ( <i>R</i> )
11	<b>10</b>	en	120	48	-	13 ( <i>R</i> )
12	<b>10</b>	ampy	120	86	1800	66( <i>R</i> )
13	<b>10</b>	( <i>R,R</i> )-DPEN	120	85	800	46 ( <i>S</i> )
14	<b>10</b>	( <i>S,S</i> )-DPEN	120	46	300	53 ( <i>R</i> )
15	<b>11</b>	en	120	85	3700	-
16	<b>12</b>	en	120	46	-	-
17	<b>13</b>	en	30	97	6000	18 ( <i>S</i> )
18	<b>13</b>	(±)- <i>i</i> Pr-ampy <sup>[c]</sup>	5	97	19000	24 ( <i>S</i> )
19	<b>13</b>	( <i>S,S</i> )-DPEN	5	96	12000	19 ( <i>S</i> )
20	<b>14</b>	en	30	91	10000	24 ( <i>R</i> )
21	<b>14</b>	( <i>R,R</i> )-DPEN	30	97	18000	12 ( <i>R</i> )
22	<b>14</b>	( <i>S,S</i> )-DPEN	30	92	15000	26 ( <i>R</i> )

<sup>a</sup> The conversion has been determined by GC analysis. <sup>b</sup> Turnover frequency (moles of ketone converted to alcohol per mole of catalyst per hour) at 50% conversion. <sup>c</sup> 2 eq. with respect to the diphosphine precursors.

**Table S2.** Further data regarding the catalytic TH of aldehydes and ketones (0.1 M) to alcohols with complexes **1**, **3-5** and **15-16** (S/C 1000) in 2-propanol at 82 °C, and in the presence of 2 mol % NaOiPr.

Entry	Complex	substrate	Time [min]	Conv. <sup>[a]</sup> [%]
1	<b>1</b>	benzaldehyde	10	11
2	<b>3</b>	benzaldehyde	10	10
3	<b>4</b>	benzaldehyde	30	8
4	<b>5</b>	benzaldehyde	60	14
5	<b>5</b>	4-bromo-benzaldehyde	60	30
6	<b>15</b>	benzaldehyde	60	20
7	<b>16</b>	benzaldehyde	60	25

<sup>a</sup>The conversions has been determined by GC analysis.

**Table S3.** Further data regarding the catalytic HY (30 bar) of ketones (2.0 M) to alcohols with complexes **2**, **15** and KO*t*Bu (2 mol%) as base in EtOH at 70 °C.

Entry	Complex	Substrate	S/C	Time [h]	Conv. <sup>[a]</sup> [%]
1	<b>2</b>	tetralone	10000	16	8
2	<b>2</b>	benzoin	10000	16	5
3	<b>15</b>	tetralone	10000	16	4
4	<b>15</b>	2'-Me-acetophenone	10000	16	28
5	<b>15</b>	4'-NO <sub>2</sub> -acetophenone	10000	16	1
6	<b>15</b>	benzoin	10000	16	9

<sup>a</sup>The conversions has been determined by GC analysis.