

## Supporting Information

### Catalytic Conversion of Ethanol to *n*-Butanol Using Ruthenium P-N Ligand Complexes

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## Experimental

### General considerations

All procedures were carried out under an inert atmosphere ( $N_2$ ) using standard Schlenk line techniques or in an inert atmosphere glovebox (Ar). Chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise stated. Solvents were purified using an anhydrous Engineering Grubbs-type solvent system except anhydrous ethanol which was purchased from Sigma-Aldrich and used as received. Ligands **1-3**,<sup>1</sup> **4**<sup>2</sup> and **5**<sup>3</sup> and complexes **6**<sup>4</sup> and **7**<sup>5</sup> were synthesised by literature methods. Complex **8** was purchased from Sigma-Aldrich and used as received. [di- $\mu$ -chloro(bis( $\eta^6$ -*p*-cymene)chlororuthenium(II))] was synthesised by a modification of a literature method replacing  $\alpha$ -phellandrene with  $\alpha$ -terpinene.<sup>6</sup> NMR spectra were recorded on Jeol ECS300, Varian 400MR and Bruker 500 Cryo NMR spectrometers.  $^1H$  and  $^{13}C\{^1H\}$  NMR chemical shifts were referenced relative to the residual solvent resonances in the deuterated solvent.  $^{31}P\{^1H\}$  NMR spectra were referenced relative to 85%  $H_3PO_4$  external standard. Infrared spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer as solid samples in air. Mass spectra (ESI) were recorded on a Bruker Daltonics microTOF II. All catalytic samples were analysed by GC-FID/MS, using a Varian 3900/Varian Saturn 2100T GC/MS, fitted with a Varian FactorFour capillary column VF-5ms, 30 m x 0.25 mm, I.D. 0.25  $\mu m$ . Method: starting oven temp 50  $^{\circ}C$ , heat to 250  $^{\circ}C$  at 20  $^{\circ}C\ min^{-1}$ , hold at 250  $^{\circ}C$  for 5 min. Gas analysis was performed by GC-TCD on a Varian 3800 Gas Chromatograph fitted with a Varian Select Permanent Gases/ $CO_2$  column, 25 m x 0.2  $\mu m$ , using ethene as a reference (70  $\mu L$  sample:30  $\mu L$  reference). Method: hold at 45  $^{\circ}C$  for 20 min.

### Catalysis

Catalytic reactions were carried out in a 300 mL Parr stainless steel autoclave with aluminium heating mantle and using magnetic stirring. A typical procedure is shown below. Full catalytic results are shown in Table S1.

#### 1) Typical in situ catalytic run

$[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$  (0.184 g, 0.300 mmol, 0.05 mol%), ligand **1** (0.137 g, 0.599 mmol, 0.1 mol%) and sodium ethoxide (2.039 g, 29.97 mmol, 5 mol%) were added to a clean oven-dried fitted glass insert within a glovebox. The glass insert was then sealed within the autoclave, before removal from the glovebox. Ethanol (35 mL, 599 mmol) was then injected into the autoclave through an inlet against a flow of nitrogen. The autoclave was sealed and placed into the pre-heated (150  $^{\circ}C$ ) aluminium heating mantle for 4 h. After the reaction run time, the autoclave was cooled to room temperature in an ice-water bath. The autoclave was vented to remove any gas generated during the reaction. A liquid sample was removed, filtered through a short plug of Celite and analyzed by GC-MS (100  $\mu L$  of sample, 25  $\mu L$  of *n*-pentanol, 1 mL MeOH).

#### 2) Typical pre-formed catalytic run

For pre-formed runs  $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$  (0.184 g, 0.300 mmol, 0.05 mol%) and **1** (0.137 g, 0.599 mmol, 0.1 mol%) was replaced with  $[RuCl(\eta^6\text{-}p\text{-cymene})(\textbf{1})]Cl$  (0.321 g, 0.599 mmol, 0.1 mol%).

#### 3) In situ catalytic runs with addition of water

As for typical in situ run except water (1.84 or 3.89 mL) was added after the addition of ethanol.

#### 4) In situ catalytic run with addition of molecular sieves

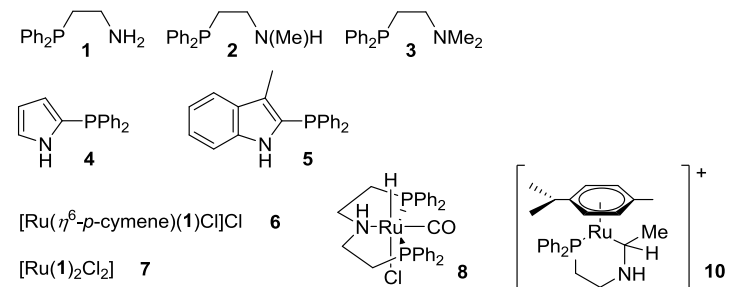
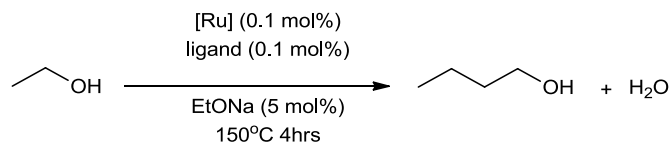
As for typical in situ run except 3Å molecular sieves (10.07 g) were added to the glass insert in the glove box after the addition of sodium ethoxide.

#### 5) Pre-formed catalytic run at low temperature and pressure

[RuCl( $\eta^6$ -*p*-cymene)(**1**)]Cl, **6** (0.321 g, 0.599 mmol, 0.1 mol%) and sodium ethoxide (2.039 g, 29.97 mmol, 5 mol%) were added to clean oven-dried glass vials within a glovebox. The low pressure Guerbet reactor (see Figure S1) was purged on a vacuum/N<sub>2</sub> line and 3Å molecular sieves were added onto the frit (17.3 g). The catalyst and base were transferred to the reactor. Ethanol (35 mL, 599 mmol) was then injected into the reactor through an inlet against a flow of nitrogen. The mixture was heated to reflux. Liquid samples were removed periodically, filtered through a short plug of Celite and analyzed by GC-MS (100  $\mu$ L of sample, 25  $\mu$ L of *n*-pentanol, 1 mL MeOH). The results of this experiment are shown in Table S2 and Figure S2.



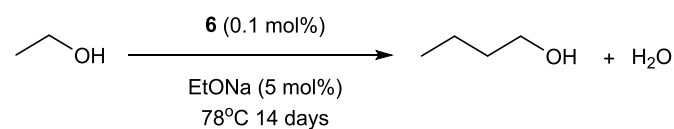
**Figure S1.** Low pressure Guerbet reactor.

**Table S1.** Ruthenium catalyzed conversion of ethanol to *n*-butanol

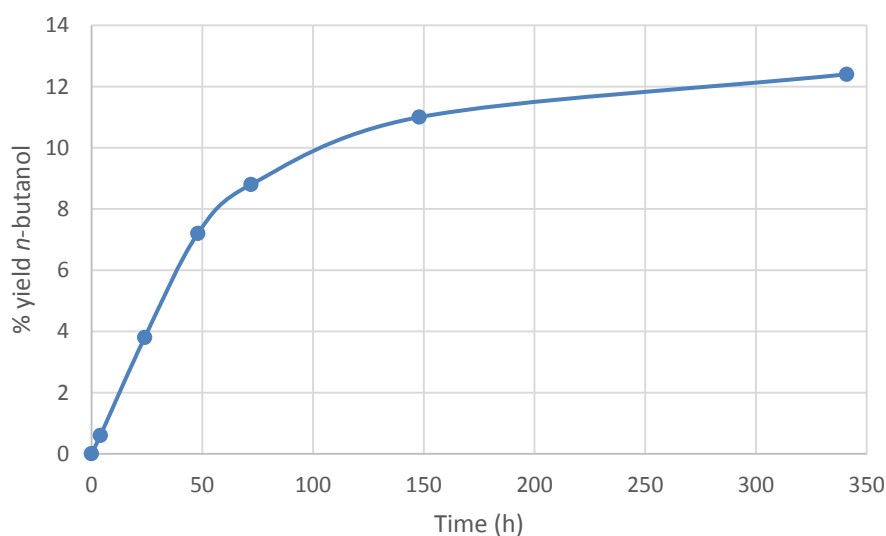
Run	[Ru]	Ligand	Conversion <sup>[a]</sup>	TON <sup>[b]</sup> (Selectivity) <sup>[c]</sup> [Yield]					
				<i>n</i> -Butanol	2-Ethylbutanol	<i>n</i> -Hexanol	2-Ethylhexanol	<i>n</i> -Octanol	EtOAc
<b>1</b>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>1</b>	25.1	219(91.1)[21.9]	7(2.0)[0.7]	25(6.9)[2.5]	-	-	-
<b>2</b> <sup>[d]</sup>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>dppm</b>	20.4	175(90.0)[17.5]	7(2.3)[0.7]	22(7.4)[2.2]	-	-	-
<b>3</b> <sup>[e]</sup>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>1</b>	9.8	98(>99)[9.8]	-	-	-	-	-
<b>4</b> <sup>[f]</sup>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>1</b>	4.9	49(>99)[4.9]	-	-	-	-	-
<b>5</b> <sup>[e]</sup>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>dppm</b>	5.7	53(95.1)[5.3]	1(1.2)[0.1]	3(3.3)[0.3]	0.2(0.2)[0.02]	0.3(0.2)[0.03]	-
<b>6</b> <sup>[f]</sup>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>dppm</b>	4.3	40(95.2)[4.0]	1(1.3)[0.1]	2(3.0)[0.2]	0.1(0.1)[0.01]	0.4(0.4)[0.04]	-
<b>7</b>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>1</b>	22.7	208(94.3)[20.8]	4(1.1)[0.4]	15(4.6)[1.5]	-	-	-
<b>8</b>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>2</b>	23.8	188(84.9)[18.8]	10(2.9)[1.0]	40(12.2)[4.0]	-	-	-
<b>9</b>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>3</b>	16.7	121(79.6)[12.1]	11(4.8)[1.1]	36(15.6)[3.6]	-	-	-
<b>10</b>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>4</b>	19.7	175(92.4)[17.5]	6(2.1)[0.6]	14(5.1)[1.4]	1(0.2)[0.1]	1(0.3)[0.1]	-
<b>11</b>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>5</b>	31.4	281(92.7)[28.1]	9(2.0)[0.9]	24(5.3)[2.4]	-	-	-
<b>12</b>	[RuCl(η <sup>6</sup> - <i>p</i> -cymene)(1)Cl], <b>6</b>	-	23.6	205(90.8)[20.5]	8(2.3)[0.8]	23(6.9)[2.3]	-	-	-
<b>13</b>	<i>trans</i> -[RuCl <sub>2</sub> (1) <sub>2</sub> ], <b>7</b>	-	18.8	171(93.5)[17.1]	3(1.0)[0.3]	12(4.2)[1.2]	-	-	2(1.3)[0.2]
<b>14</b> <sup>[g]</sup>	[RuCl <sub>2</sub> (η <sup>6</sup> - <i>p</i> -cymene)] <sub>2</sub>	<b>1</b>	20.5	180(91.7)[18.0]	9(3.2)[0.9]	15(5.2)[1.5]	-	-	-
<b>15</b>	Ru-MACHO®, <b>8</b>	-	13.3 <sup>[h]</sup>	16(12.4)[1.6]	0.4(0.2)[0.04]	0.3(0.2)[0.03]	-	-	54(40.6)[5.4]
<b>16</b>	<b>10</b>	-	21.1	195(95.1)[19.5]	3(1.0)[0.3]	10(3.2)[1.0]	1(0.2)[0.1]	2(0.4)[0.2]	-

[a] Total conversion of ethanol to liquid products, *n*-butanol, 2-ethylbutanol, *n*-hexanol, 2-ethylhexanol, *n*-octanol and Ethyl acetate. [b] TON based on mmol of substrate converted to products per mmol of Ru. [c] Total selectivity to products in the liquid fraction determined by GC. [d] Data taken from reference 12 (main text). [e] 1.84 ml water added (5% by volume). [f] 3.89 ml water added (10% by volume). [g] 10 g 3Å molecular sieves added. [h] Other products 6.2%.

**Table S2.** Ruthenium catalyzed conversion of ethanol to *n*-butanol in low temperature/pressure apparatus



Time elapsed (h)	<i>n</i> -Butanol yield (%)	Selectivity (%)
4	0.6	96.7
24	3.8	94.2
48	7.2	92.5
72	8.8	92.6
148	11.0	92.9
341	12.4	92.7



**Figure S2.** Plot of *n*-butanol yield vs time for low temperature/pressure run.

## 6) Kinetic plot experiments

A kinetic plot for complex **6** was generated by performing autoclave runs as in the typical pre-formed catalytic run above but stopping the reactions at certain times. The kinetic plot runs were performed in a 100 mL Parr autoclave using [RuCl( $\eta^6$ -*p*-cymene)(**1**)]Cl, **6** (0.092 g, 0.171 mmol, 0.1 mol%), sodium ethoxide (0.583 g, 8.56 mmol, 5 mol%) and ethanol (10 mL, 171 mmol). The results are shown in Table S3 and Figure S3.

## 7) Solid analysis

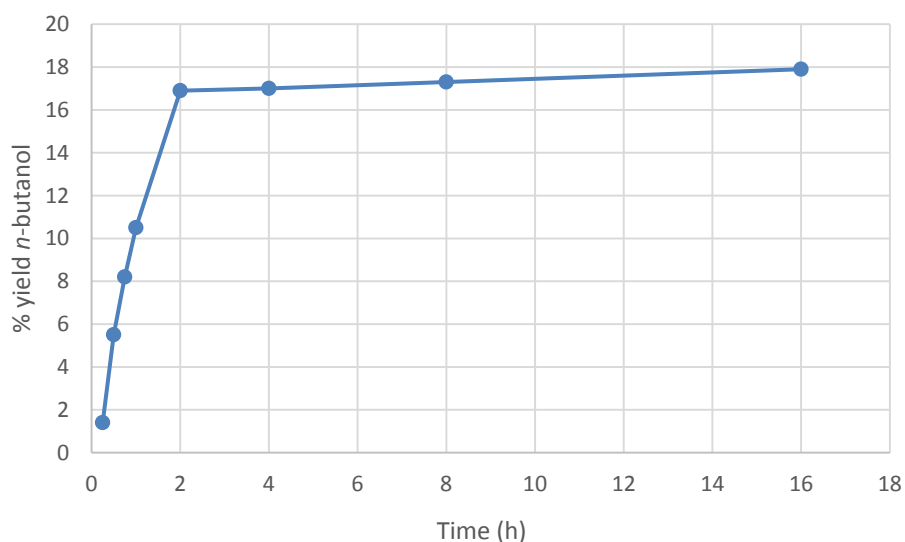
After a catalytic run all volatiles were removed on a rotavap. The solid product was scraped into a powder and dried for several days on a vacuum line. DCM was added (40 mL) and the mixture was stirred for 1h. The solvent was removed by filtration and the solid was dried for several days on a vacuum line. A weighed sample of the solid was dissolved in methanol-*d*<sub>4</sub> and filtered through a Pasteur pipette containing a glass filter paper. A known amount of dmso was added as a reference and the solution was analysed by <sup>1</sup>H NMR spectroscopy. A typical spectrum is shown in Figure S31.

**Table S3.** Ruthenium catalyzed conversion of ethanol to *n*-butanol using catalyst **6** over time

CCO
 $\xrightarrow[\text{EtONa (5 mol\%)}]{\textbf{6 (0.1 mol\%)}}$ 
CCCCO + H<sub>2</sub>O

150°C 42.5 h

Time elapsed (h)	<i>n</i> -Butanol yield (%)	Selectivity (%)
0.25	1.4	>99
0.5	5.5	97.1
0.75	8.2	95.3
1	10.5	95.8
2	16.9	93.6
4	17.0	92.5
8	17.3	92.7
16	17.9	92.2
42.5	17.4	91.5

**Figure S3.** Plot of *n*-butanol yield vs time for catalyst **6** performed in an autoclave

### Catalyst monitoring experiments

#### 1) Monitoring by ESI-MS

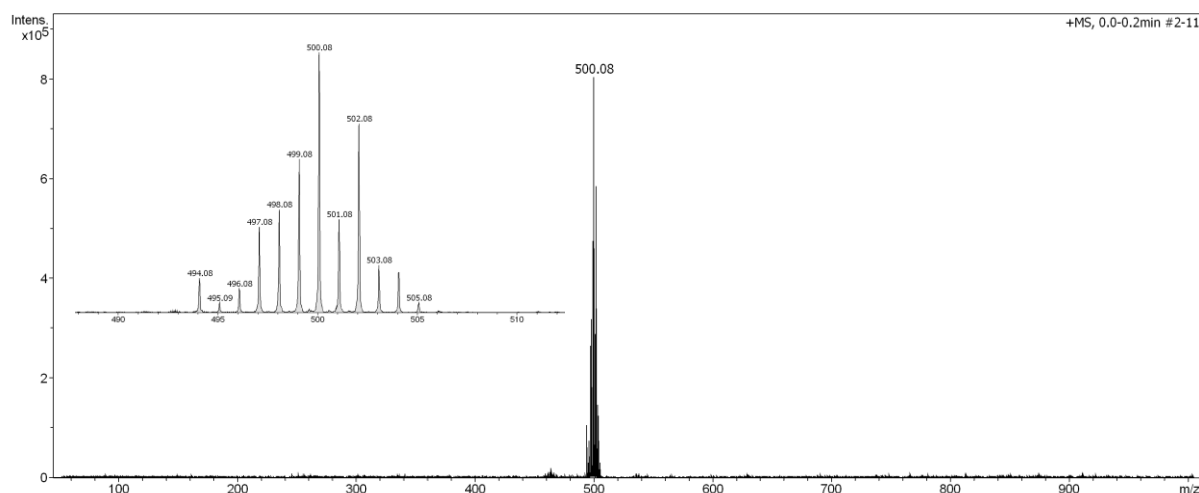
[RuCl( $\eta^6$ -*p*-cymene)(**1**)]Cl, **6** (0.178 g, 0.332 mmol, 0.1 mol%) was dissolved in ethanol (15 mL) in a Schlenk flask to give an orange solution. A 0.1 mL sample was removed for analysis (see below). A solution of sodium ethoxide (0.226 g, 3.32 mmol, 1 mol%) in ethanol (4.4 mL) was added to the solution of **6** which rapidly turned cloudy. The mixture was stirred for 1 h and then filtered into the low pressure Guerbet reactor (see Figure S1). A 0.1 mL sample was removed for analysis. The reaction mixture was heated to reflux and 0.1 mL samples were removed periodically for analysis. **Sample analysis:** Samples were kept under nitrogen until just before analysis when they were opened to air and diluted with ethanol/water before being injected into the spectrometer. ESI-MS Spectra are shown in Figures S4-S17.

## 2) Monitoring by NMR spectroscopy and Isolation of complex 10

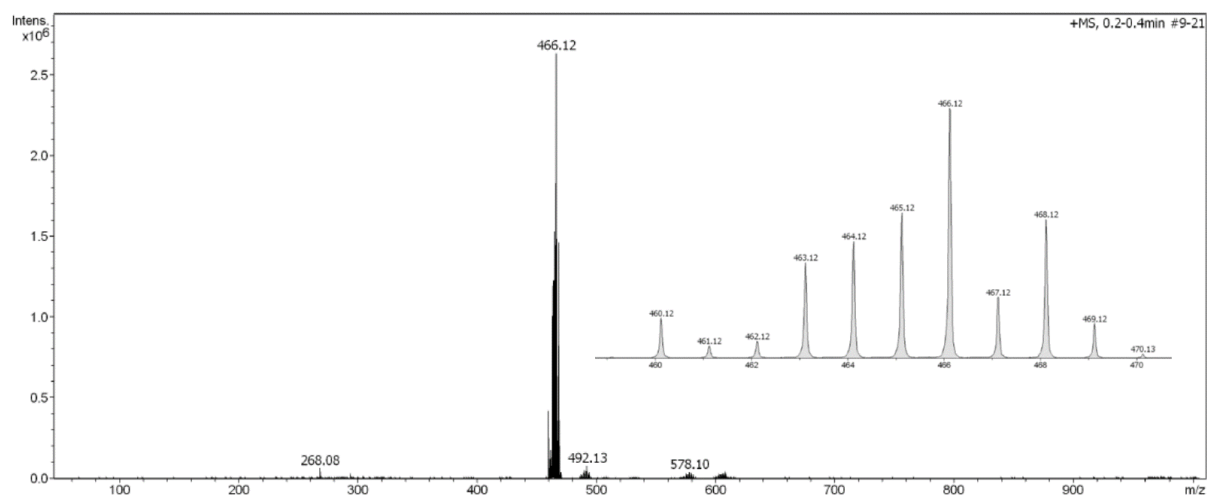
[RuCl( $\eta^6$ -*p*-cymene)(1)]Cl, **6** (0.092 g, 0.171 mmol, 0.1 mol%) was dissolved in ethanol (5 mL) in a Schlenk flask to give an orange solution. A 0.7 mL sample was removed for analysis by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy (see Figure S18). A solution of sodium ethoxide (0.117 g, 1.713 mmol, 1 mol%) in ethanol (3 mL) was added to the solution of **6** which rapidly turned cloudy. Further ethanol (2 mL) was used to wash in any residual sodium ethoxide solution making the total volume of ethanol 10 mL (171.26 mmol). The mixture was stirred for 1 h and a 0.7 mL sample was removed for analysis by  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectroscopy which showed the formation of hydride species **9** (see Figures S20-21). The mixture was stirred for 40 min while heating to reflux (attained after 25 min). After cooling the mixture was filtered and the volatiles were removed *in vacuo* to give a brown powder. Hexane (20 mL) was added and the mixture was heated gently to obtain an orange solution and some brown solid. The solution was filtered and the volatiles were removed *in vacuo* to give **10** as a brown powder (0.060 g, 0.114 mmol, 66% yield, assuming chloride counterion). NMR spectra are shown in Figures S22-S30.

[Ru( $\eta^6$ -*p*-cymene)(Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>NHCHCH<sub>3</sub>)]<sup>+</sup> (**10**):  $^{31}\text{P}\{^1\text{H}\}$  NMR (CD<sub>3</sub>OD, 121.7 MHz)  $\delta$  72.94.  $^1\text{H}$  NMR (CD<sub>3</sub>OD, 300 MHz)  $\delta$  1.16 (3H, d,  $J$  = 6.9 Hz, CHCH<sub>3</sub>), 1.21 (3H, d,  $J$  = 6.9 Hz, CHCH<sub>3</sub>), 1.64 (3H, d, 5.8 Hz, RuCHCH<sub>3</sub>), 1.73 (1H, m,  $J$  = 15.7, 7.8, 4.4 Hz, PCHH), 2.12-2.25 (2H, m, CH(CH<sub>3</sub>)<sub>2</sub> and RuCHCH<sub>3</sub>), 2.28 (3H, s, cym-CH<sub>3</sub>), 2.48 (1H, m,  $J$  = 15.7, 11.7, 6.8 Hz, PCHH), 3.09 (1H, m,  $J$  = 12.1, 7.8, 1.9 Hz, NCHH), 3.52 (1H, m,  $J$  = 33.8, 11.9, 7.1 Hz, NCHH), 4.87 (1H, d,  $J$  = 6.0 Hz, cym-CH), 5.12 (1H, d,  $J$  = 6.1 Hz, cym-CH), 5.31 (1H, d,  $J$  = 6.0 Hz, cym-CH), 5.40 (1H, d,  $J$  = 6.1 Hz, cym-CH), 7.27-7.40 (2H, m, ArH), 7.47-7.59 (6H, m, ArH), 7.64-7.71 (2H, m, ArH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD<sub>3</sub>OD, 125.8 MHz)  $\delta$  19.7 (cym-CH<sub>3</sub>), 23.2 (RuCHCH<sub>3</sub>), 24.2 (CHCH<sub>3</sub>), 24.3 (d,  $J$  = 24.2 Hz, PCH<sub>2</sub>), 24.4 (CHCH<sub>3</sub>), 32.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 42.3 (d,  $J$  = 9.7 Hz, RuCHCH<sub>3</sub>), 53.11 (d,  $J$  = 3.5 Hz, NCH<sub>2</sub>), 84.3 (d,  $J$  = 4.4 Hz, cym-CH), 84.6 (d,  $J$  = 1.5 Hz, cym-CH), 90.8 (d,  $J$  = 1.8 Hz, cym-CH), 92.3 (d,  $J$  = 4.3 Hz, cym-CH), 102.4 (cym-CMe), 114.3 (cym-C<sup>i</sup>Pr), 131.1, 131.1, 131.1, 131.2, 129.8, 129.9, 129.9, 129.9, 132.5, 132.5, 134.7 (d,  $J$  = 48.6 Hz, Ar-CP), 135.0 (Ar-CH), 135.1 (Ar-CH), 140.9 (d,  $J$  = 47.5 Hz, Ar-CP). IR (solid) 2950 (m), 2792 (m), 2673 (m), 2579 (w), 1896 (w), 1748 (w), 1574 (s), 1435 (s), 1380 (s), 1113 (vs), 1048 (vs), 876 (s), 797 (m, split), 742 (m), 695 (s). HRMS(ESI) calculated for C<sub>26</sub>H<sub>33</sub>NPRu: 492.1396, found 492.1396. Satisfactory elemental analysis could not be obtained.

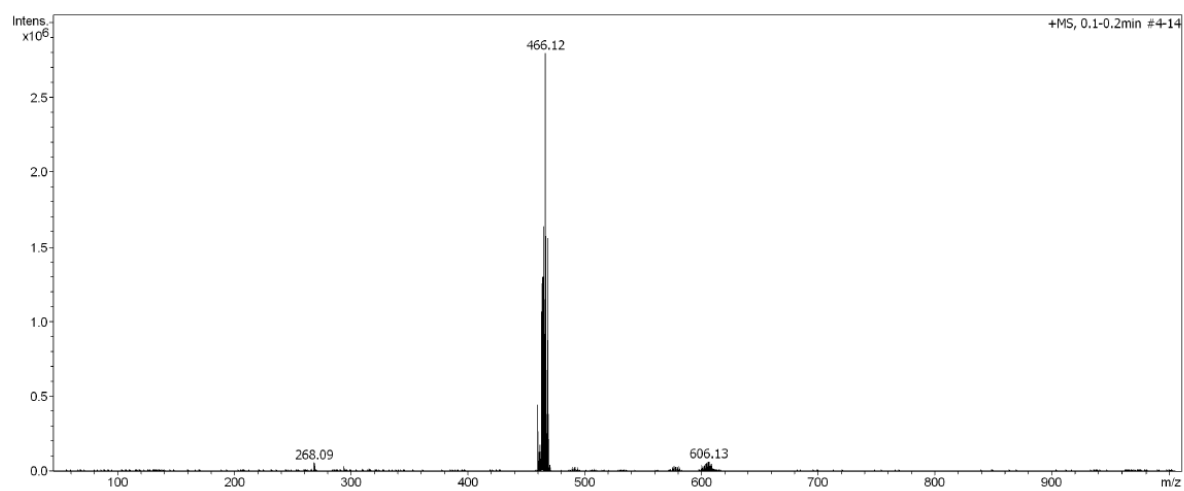
### Spectra



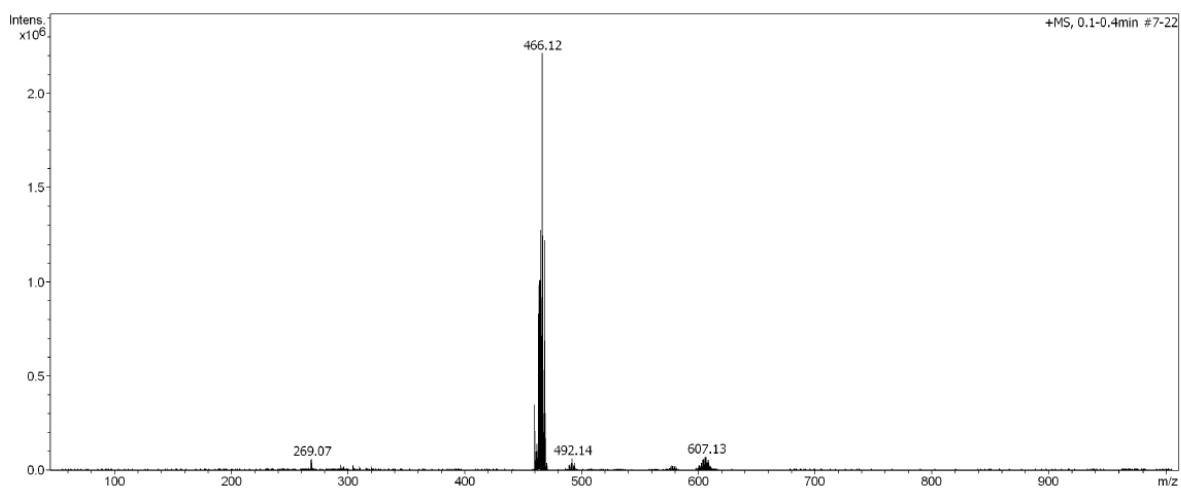
**Figure S4.** ESI-MS pre-catalyst **6** ( $m/z$ ): 500.08 [RuCl( $\eta^6$ -*p*-cymene)(1)]<sup>+</sup> (exact mass 500.08), 464.10 [Ru( $\eta^6$ -*p*-cymene)(Ph<sub>2</sub>P(CH<sub>2</sub>)<sub>2</sub>NH)]<sup>+</sup> (exact mass 464.11)



**Figure S5.** ESI-MS post base addition ( $m/z$ ): 466.12 [RuH( $\eta^6$ -*p*-cymene)(**1**)]<sup>+</sup> (exact mass 466.12)

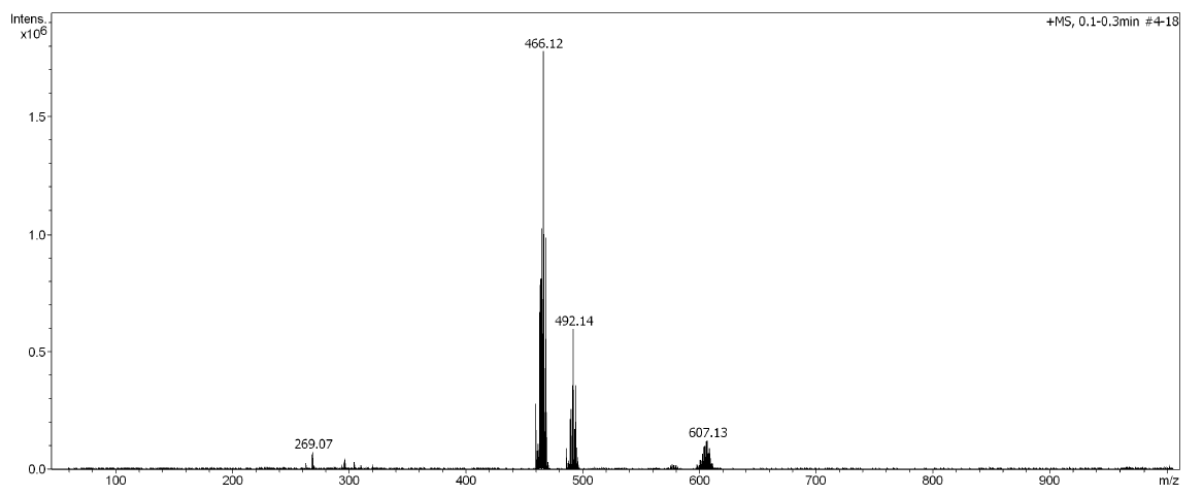


**Figure S6.** ESI-MS, 5 min, oil bath temperature, 45 °C

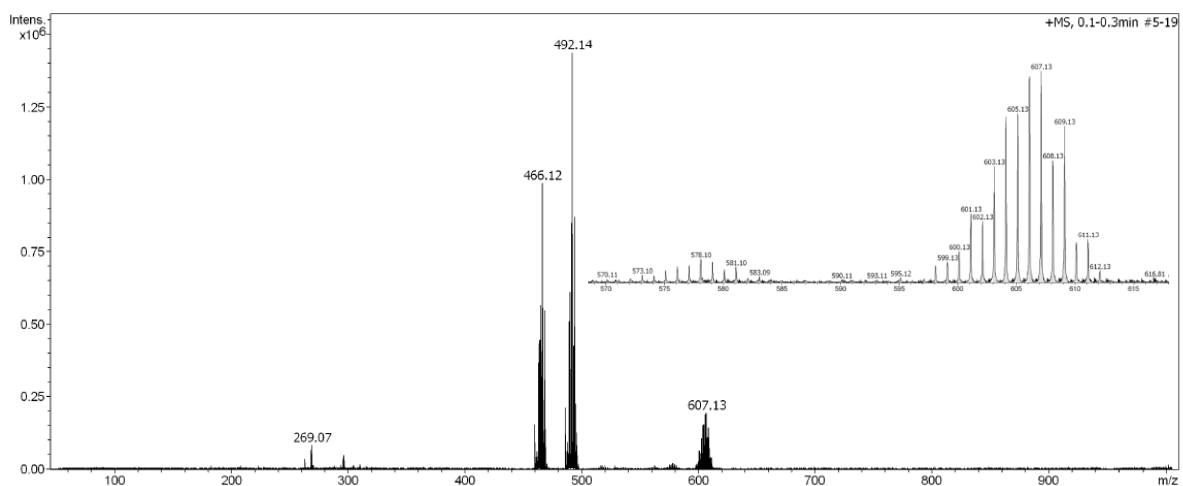


**Figure S7.** ESI-MS, 10 min, oil bath temperature, 70 °C

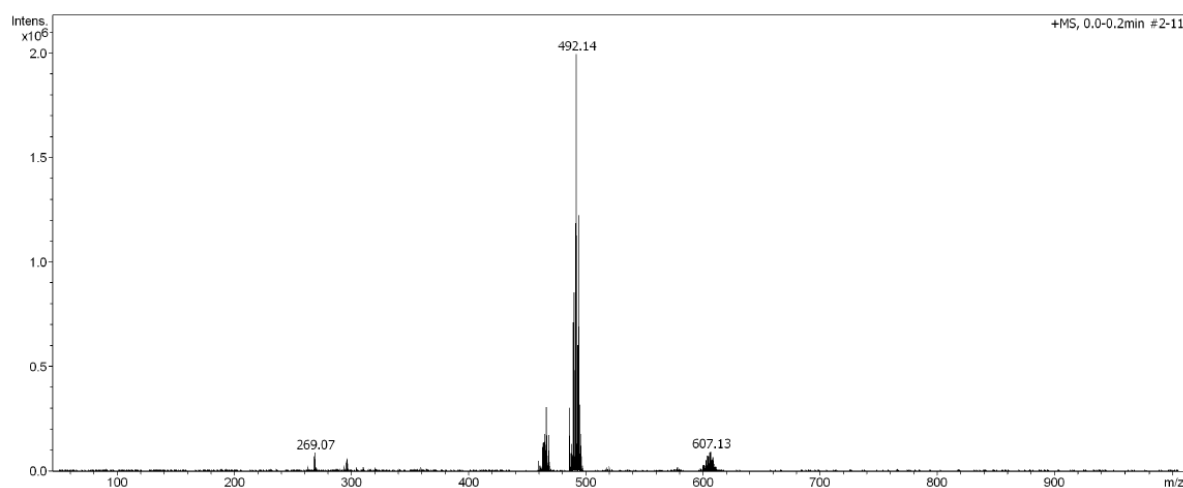




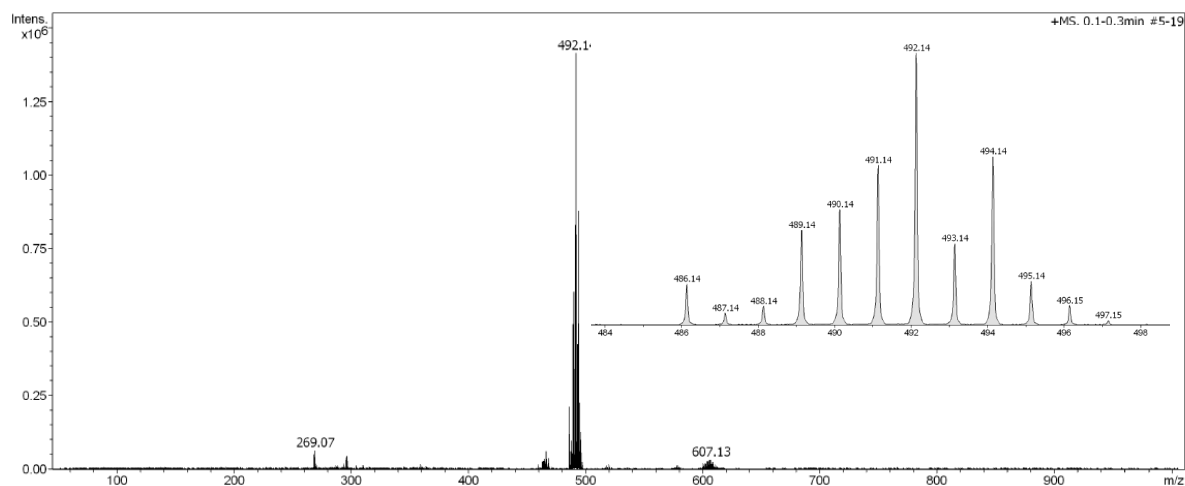
**Figure S8.** ESI-MS, 15 min, reflux ( $m/z$ ): 492.14  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{NHCHCH}_3)]^+$  (exact mass 492.14), 607.13 bimetallic species  $[\text{Ru}_2(\eta^6\text{-}p\text{-cymene})_2(\text{OEt})_3]^+$  (exact mass 607.13)



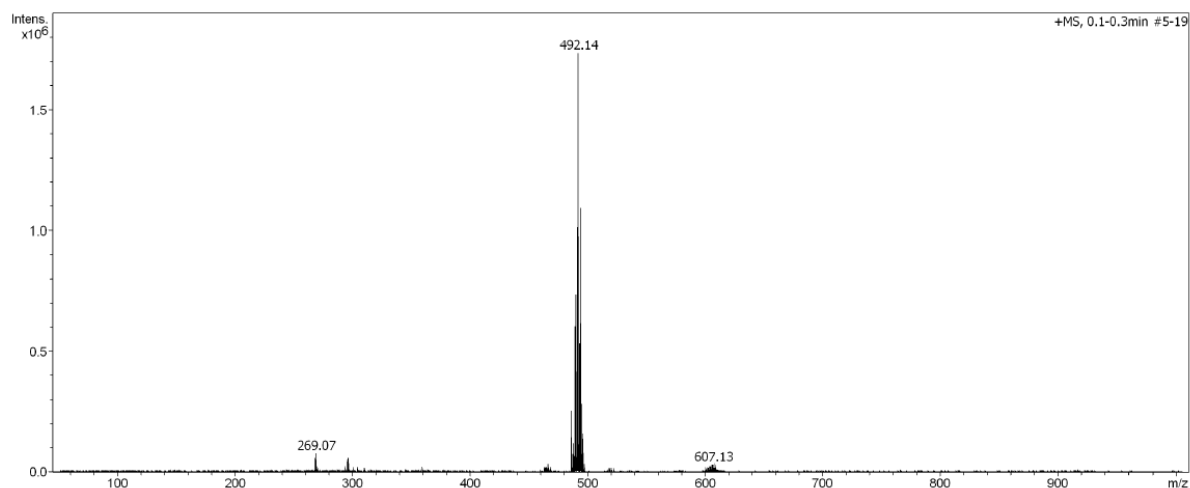
**Figure S9.** ESI-MS, 20 min, reflux ( $m/z$ ): 607.13 bimetallic species  $[\text{Ru}_2(\eta^6\text{-}p\text{-cymene})_2(\text{OEt})_3]^+$  (exact mass 607.13)



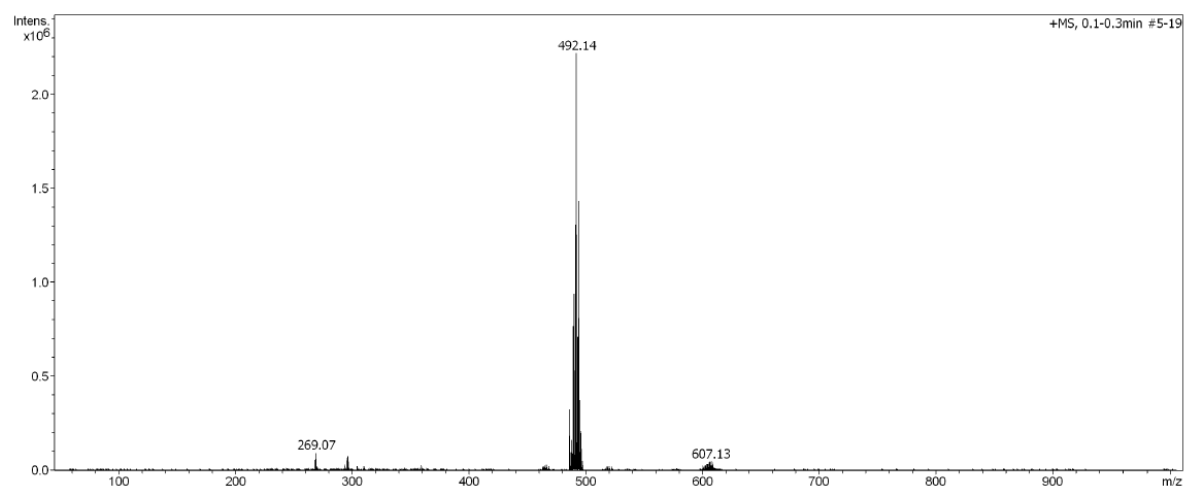
**Figure S10.** ESI-MS, 25 min, reflux



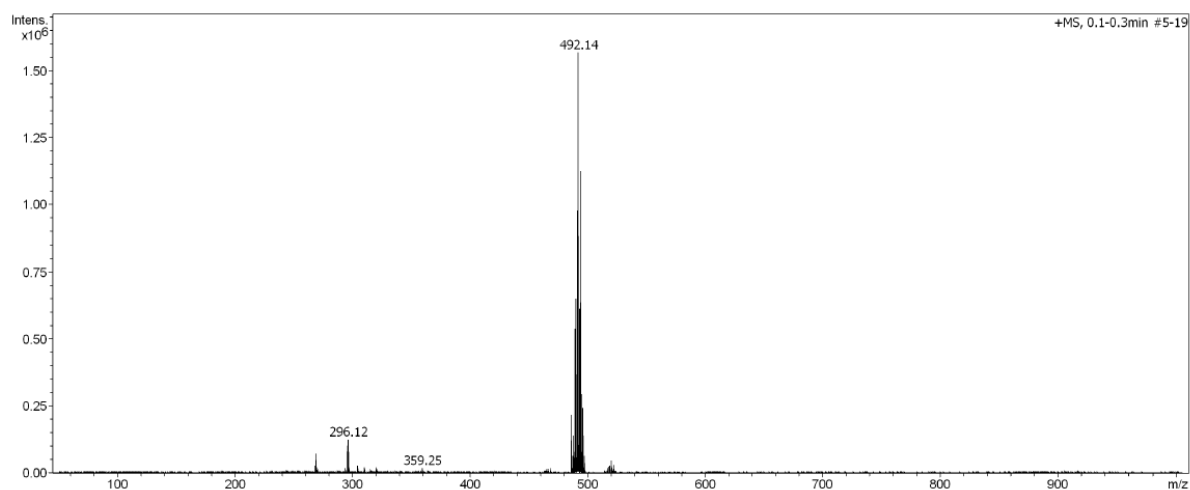
**Figure S11.** ESI-MS, 30 min, reflux ( $m/z$ ): 492.14 [ $\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{NHCHCH}_3)]^+$  (exact mass 492.14)



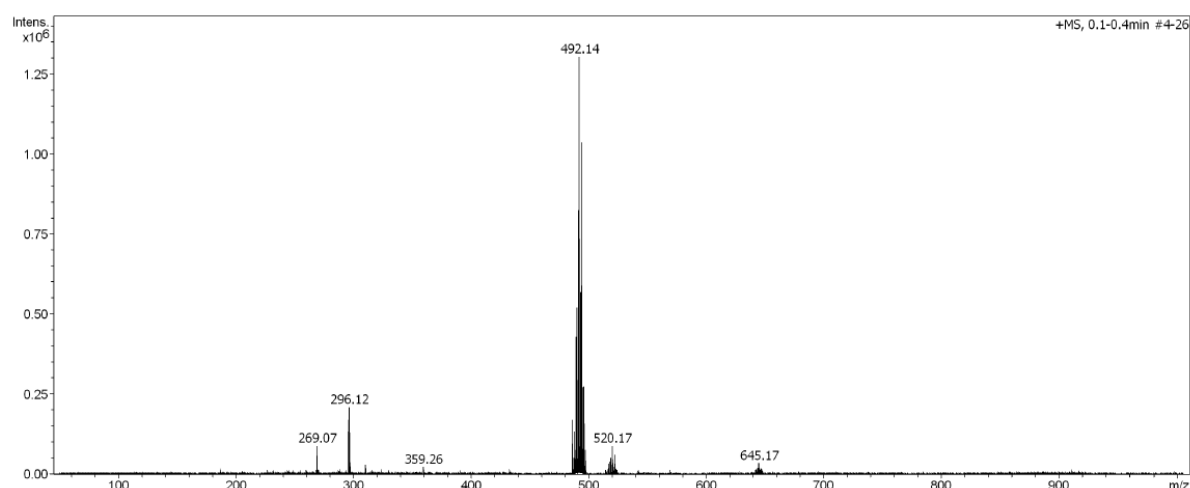
**Figure S12.** ESI-MS, 35 min, reflux



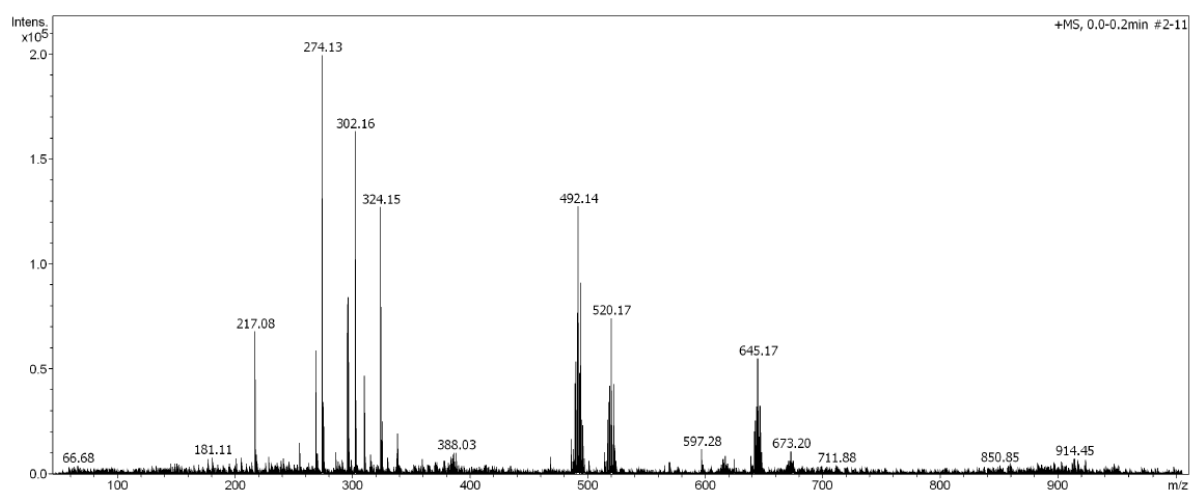
**Figure S13.** ESI-MS, 40 min, reflux



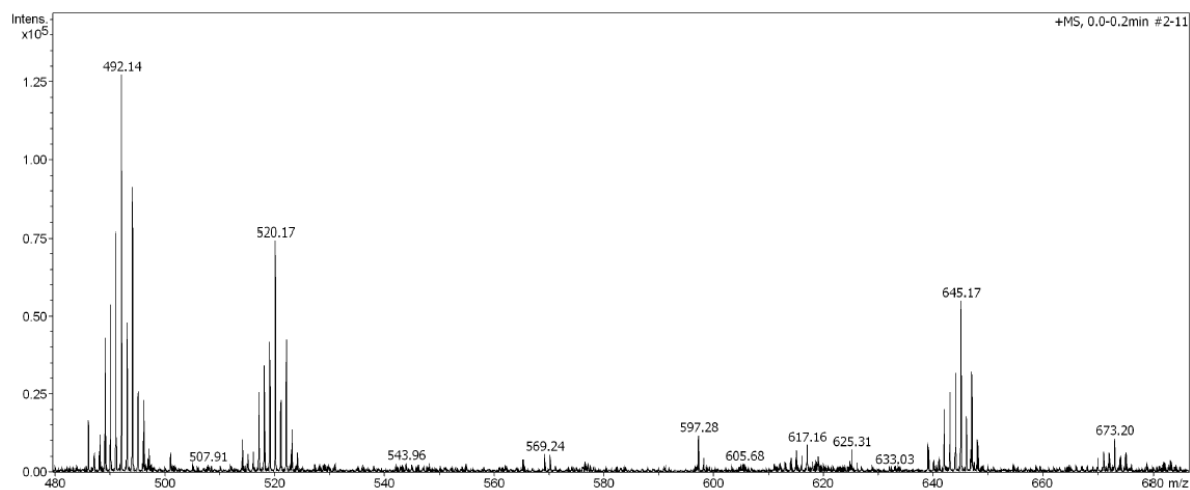
**Figure S14.** ESI-MS, 100 min, reflux



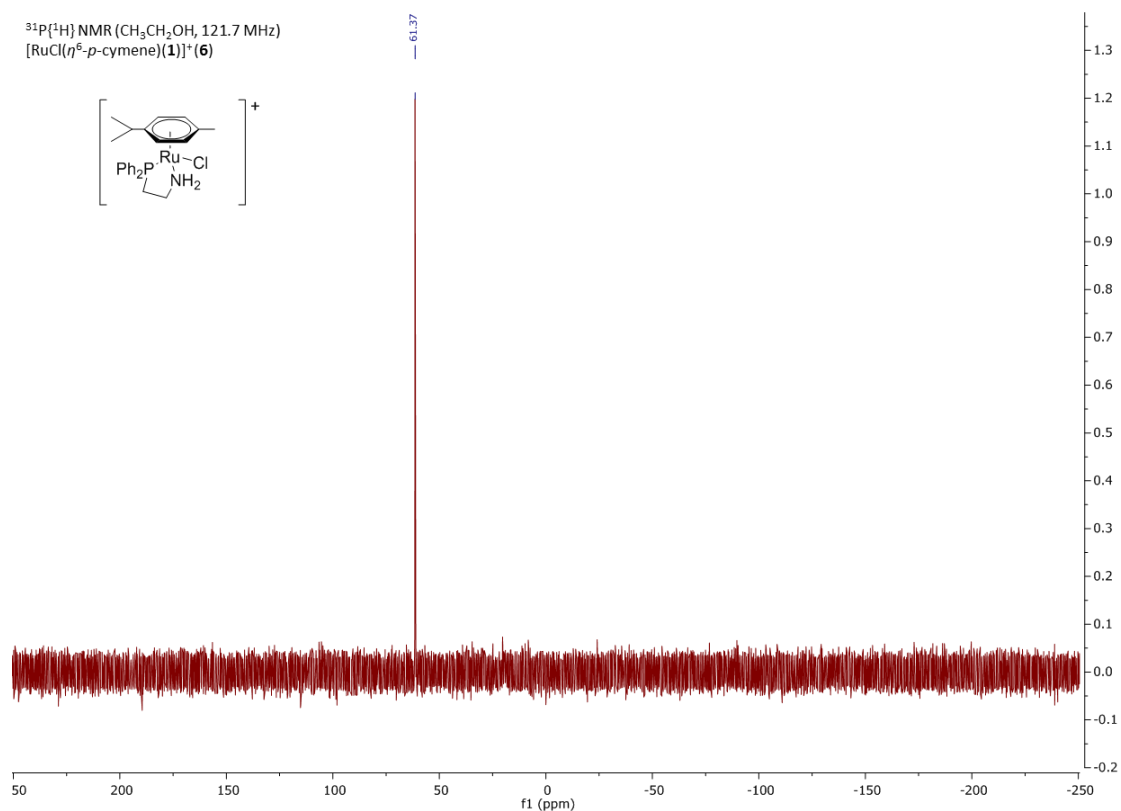
**Figure S15.** ESI-MS, 220 min, reflux ( $m/z$ ): 520.17  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{NHCHCH}_3)]^+ + \text{C}_2\text{H}_4$  (exact mass 520.17)



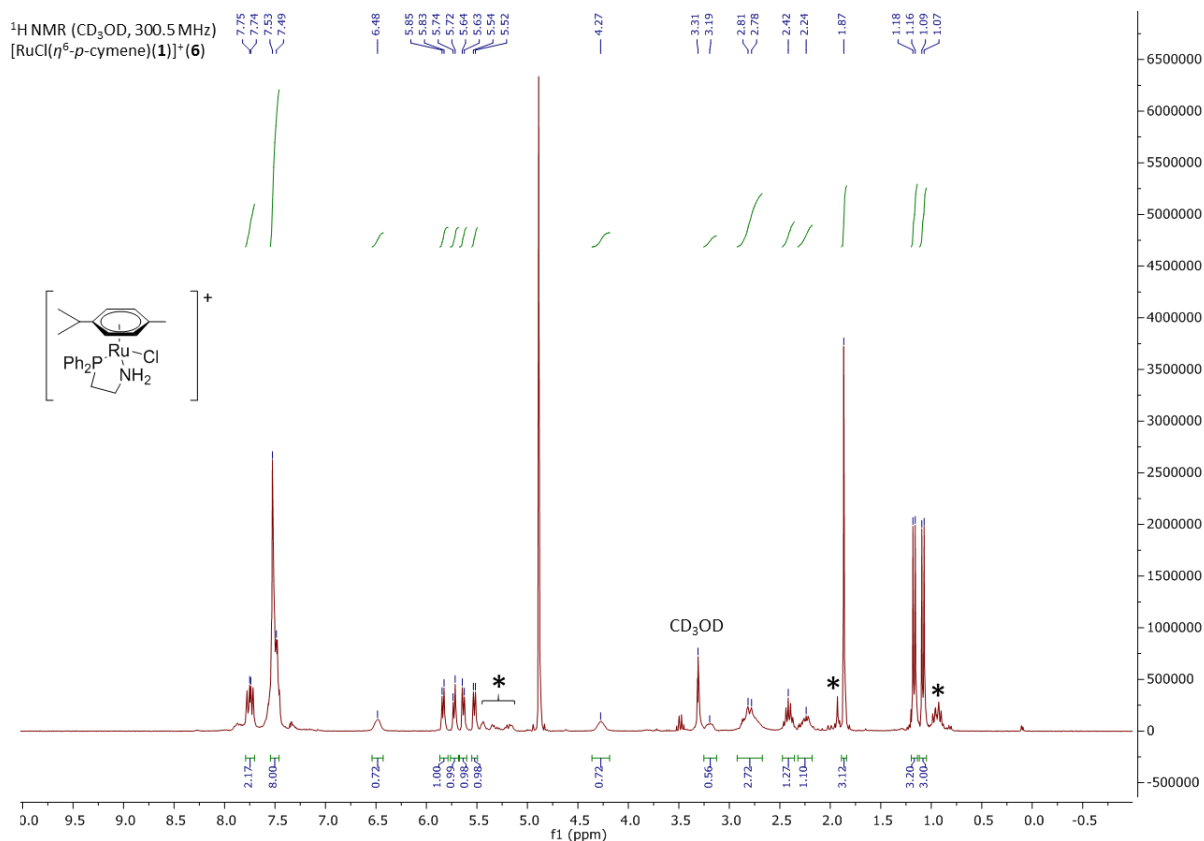
**Figure S16.** ESI-MS, 1320 min, reflux ( $m/z$ ): 645.17  $[\text{Ru}(\mathbf{1})_2] + \text{C}_4\text{H}_5\text{O}_2$  (exact mass 645.14)



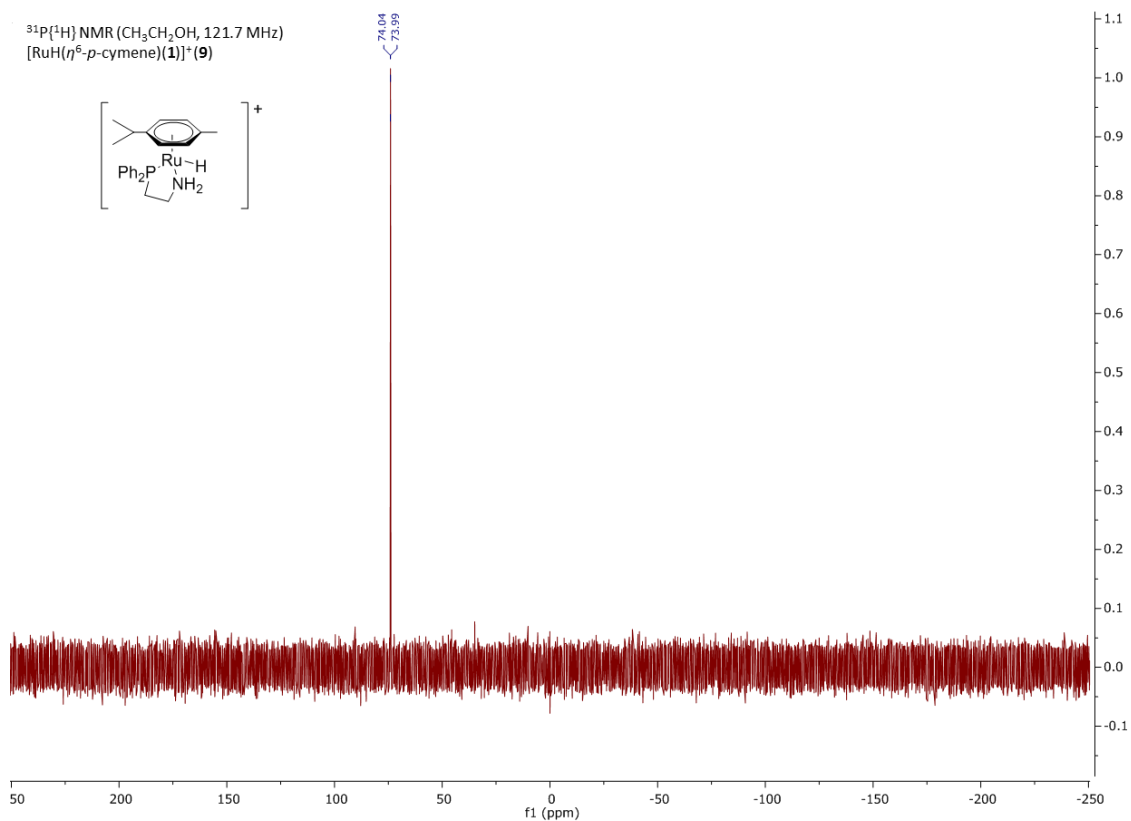
**Figure S17.** ESI-MS, 1320 min, reflux ( $m/z$ ): expansion



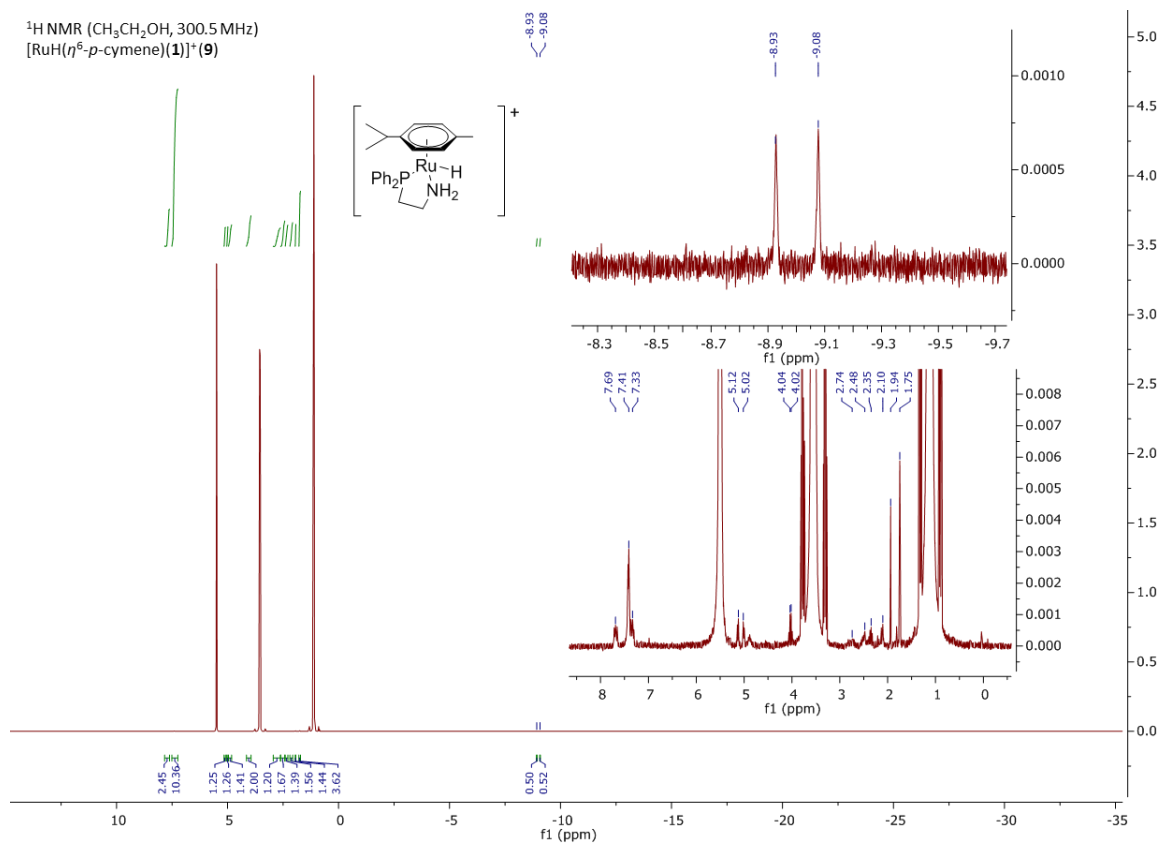
**Figure S18.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{1})]\text{Cl}$  (**6**) in ethanol (unlocked)



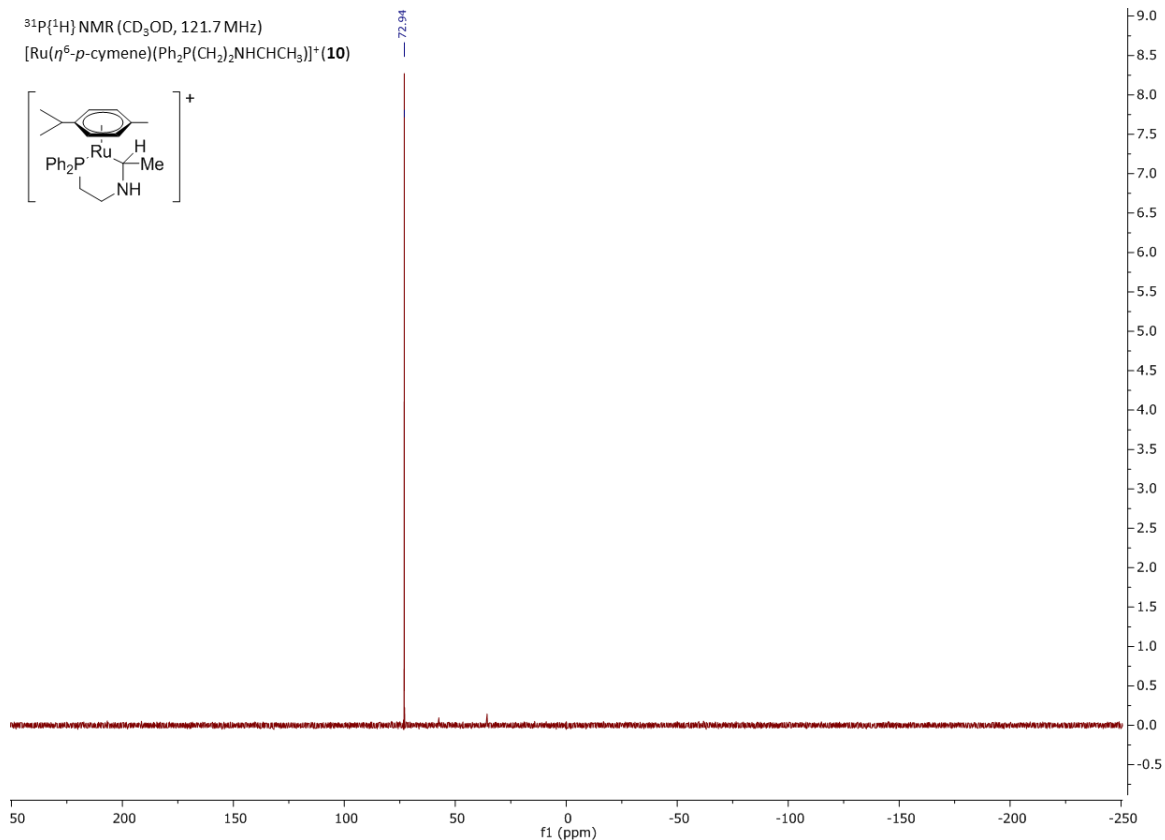
**Figure S19.**  $^1\text{H}$  NMR spectrum of  $[\text{RuCl}(\eta^6\text{-}p\text{-cymene})(\mathbf{1})]\text{Cl}$  (**6**) in methanol- $d_4$ . \* A small amount of the complex  $[\text{RuCl}_2(\eta^6\text{-}p\text{-cymene})(\kappa^1\text{-P}\mathbf{1})]$  is present



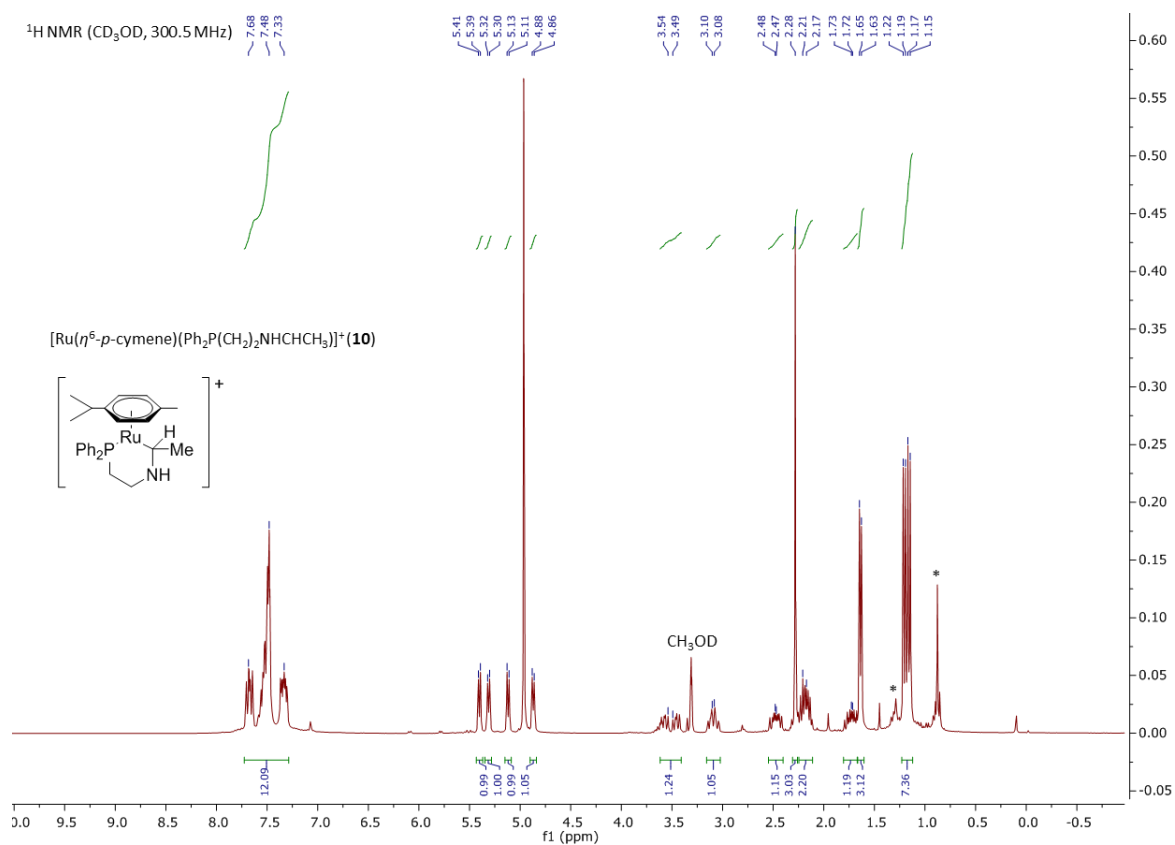
**Figure S20.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{RuH}(\eta^6\text{-}p\text{-cymene})(\mathbf{1})]$  (**9**) in ethanol (unlocked)



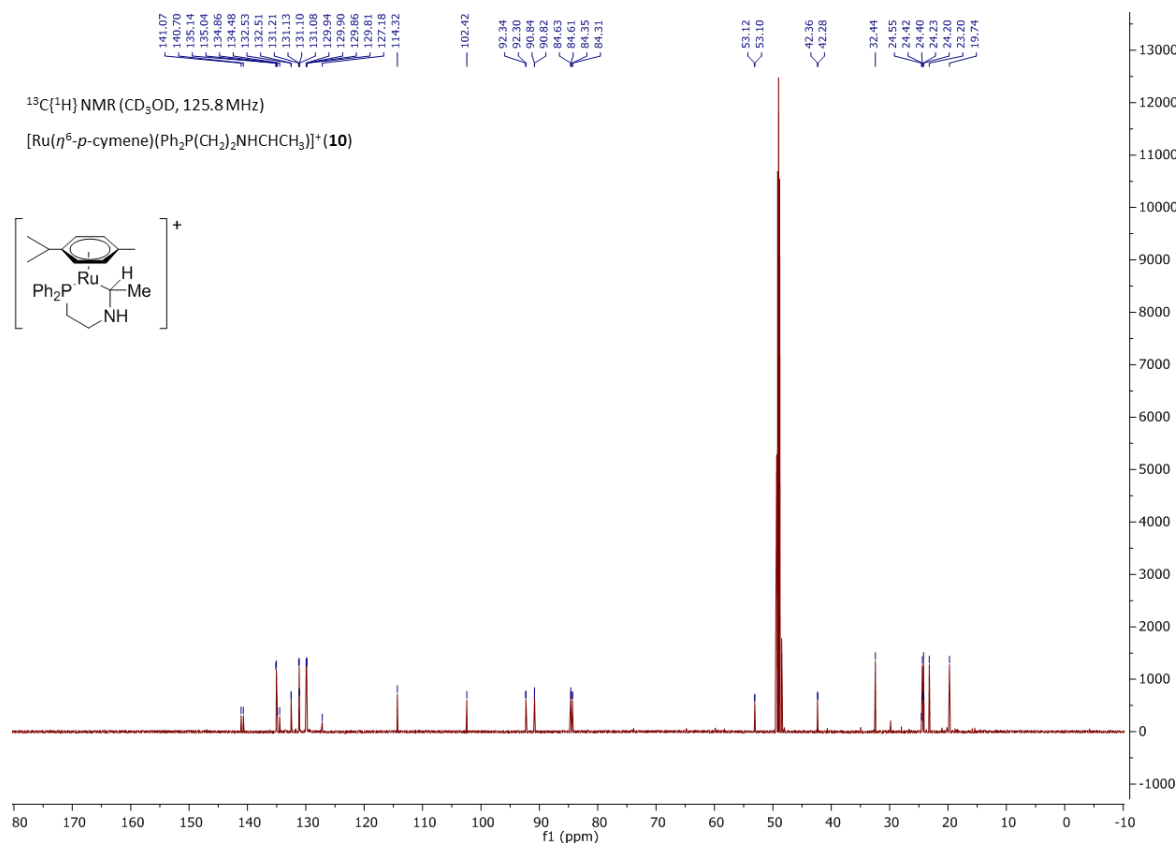
**Figure S21.**  $^1\text{H}$  NMR spectrum of  $[\text{RuH}(\eta^6\text{-}p\text{-cymene})(\mathbf{1})]^+$  ( $\mathbf{9}$ ) in ethanol (unlocked)



**Figure S22.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{NHCHCH}_3)]^+$  ( $\mathbf{10}$ ) in methanol- $d_4$



**Figure S23.**  $^1\text{H}$  NMR spectrum of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2(\text{CH}_2)_2\text{NHCHCH}_3)]^+ \text{ (10)}$  in methanol- $d_4$ .  
\*hexane peaks



**Figure S24.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2(\text{CH}_2)_2\text{NHCHCH}_3)]^+ \text{ (10)}$  in methanol- $d_4$

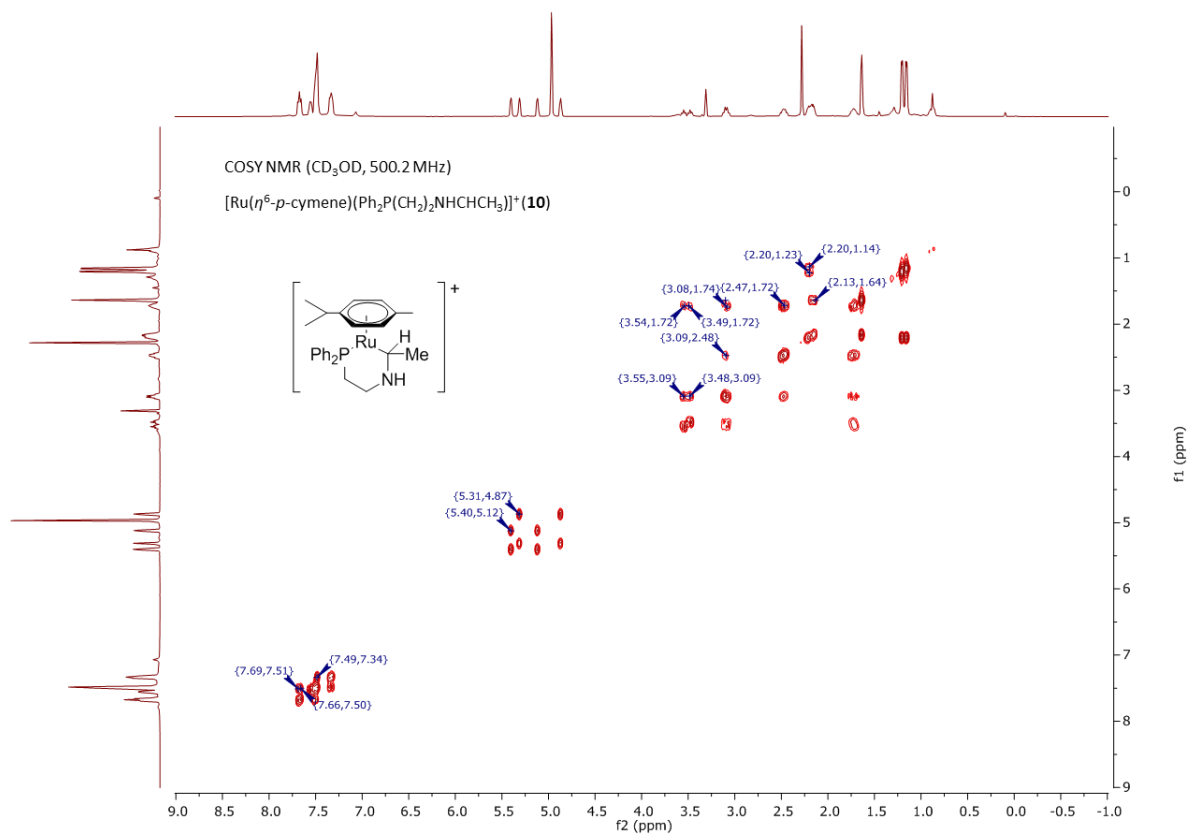


Figure S25. COSY NMR spectrum of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2(\text{CH}_2)_2\text{NHCHCH}_3)]^+ \text{ (10)}$  in methanol- $d_4$

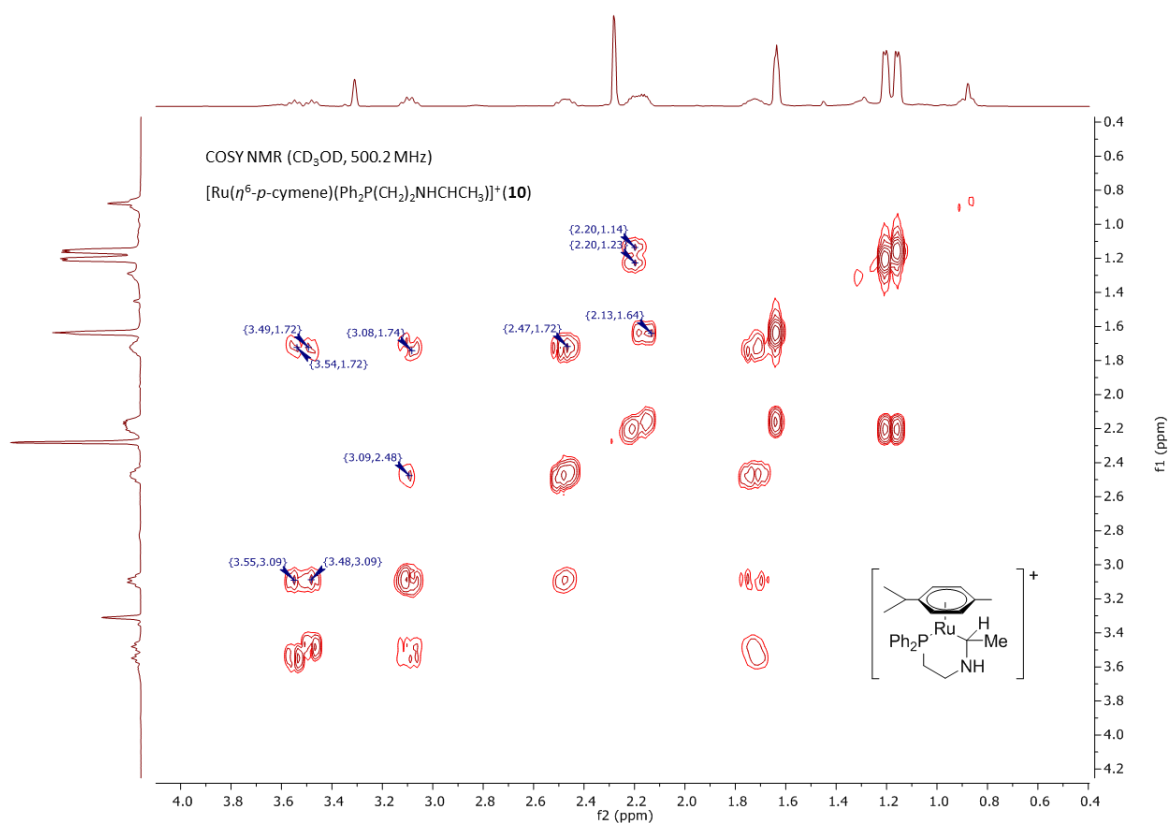
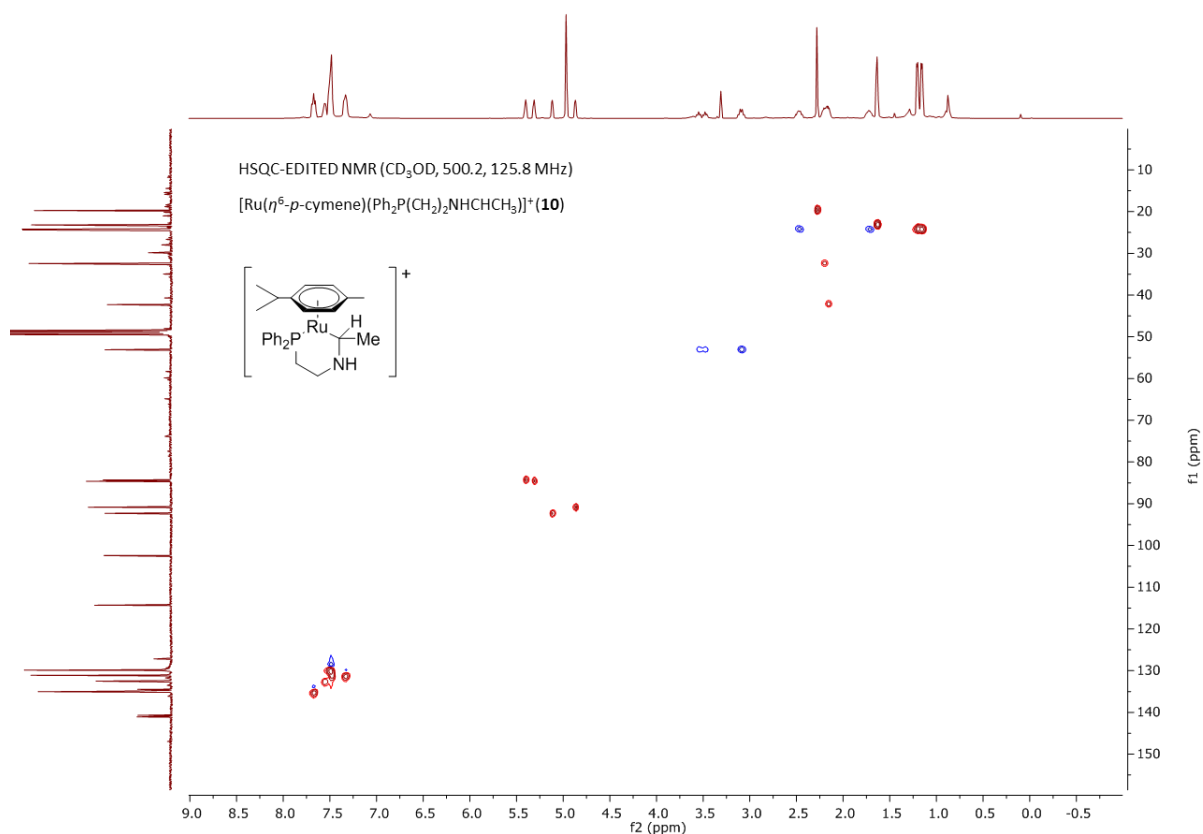
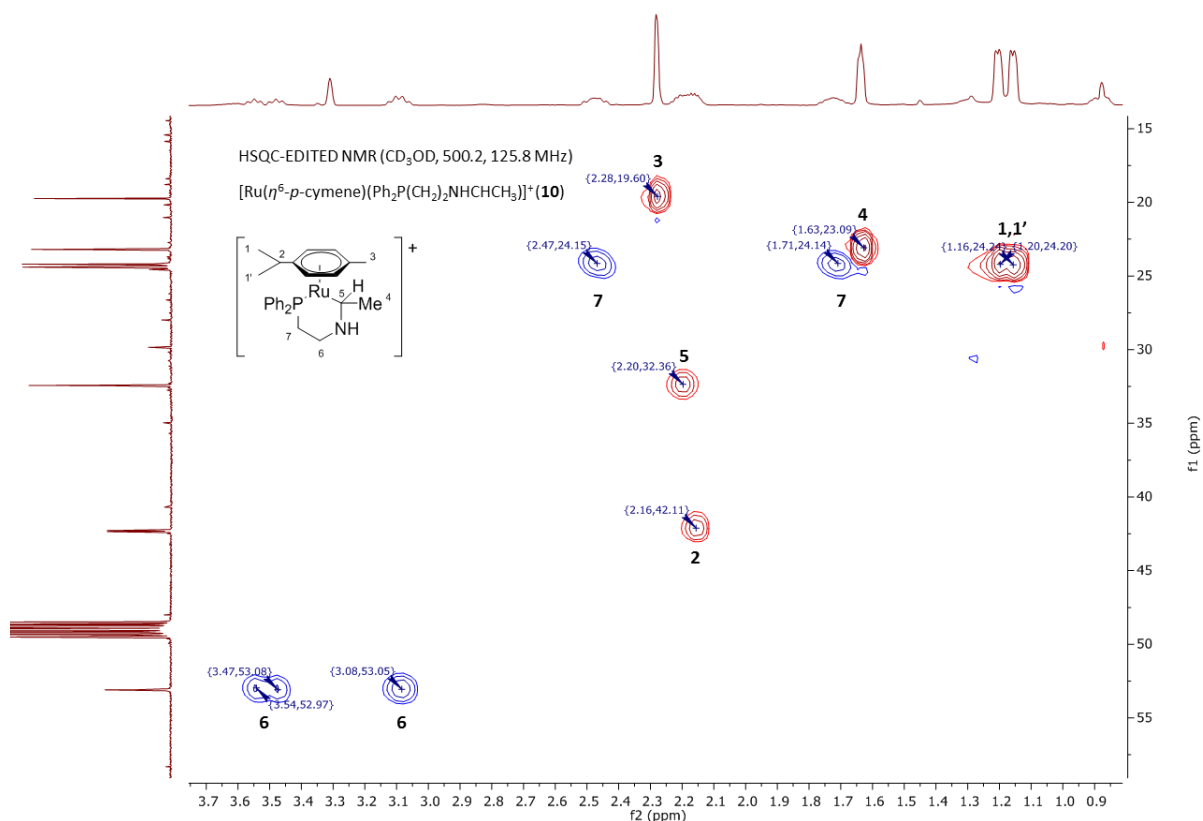


Figure S26. COSY NMR spectrum expansion of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2(\text{CH}_2)_2\text{NHCHCH}_3)]^+ \text{ (10)}$  in methanol- $d_4$

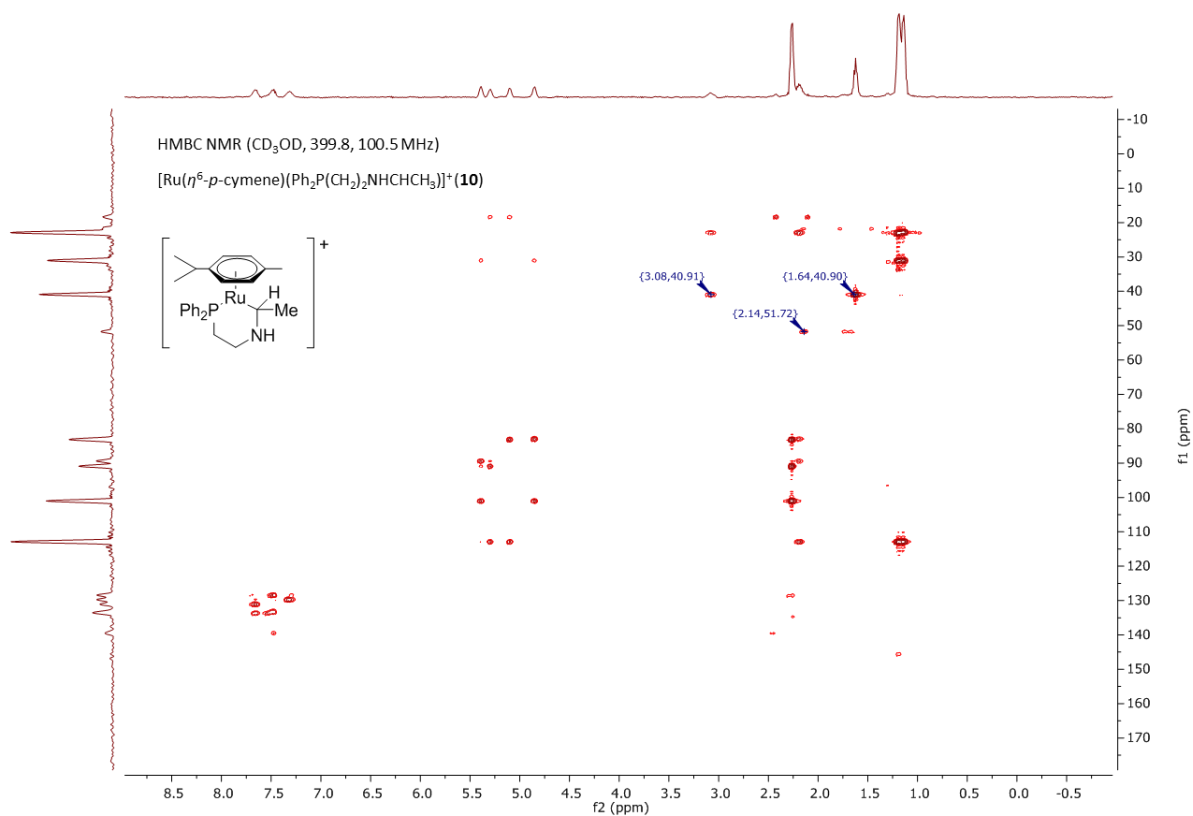




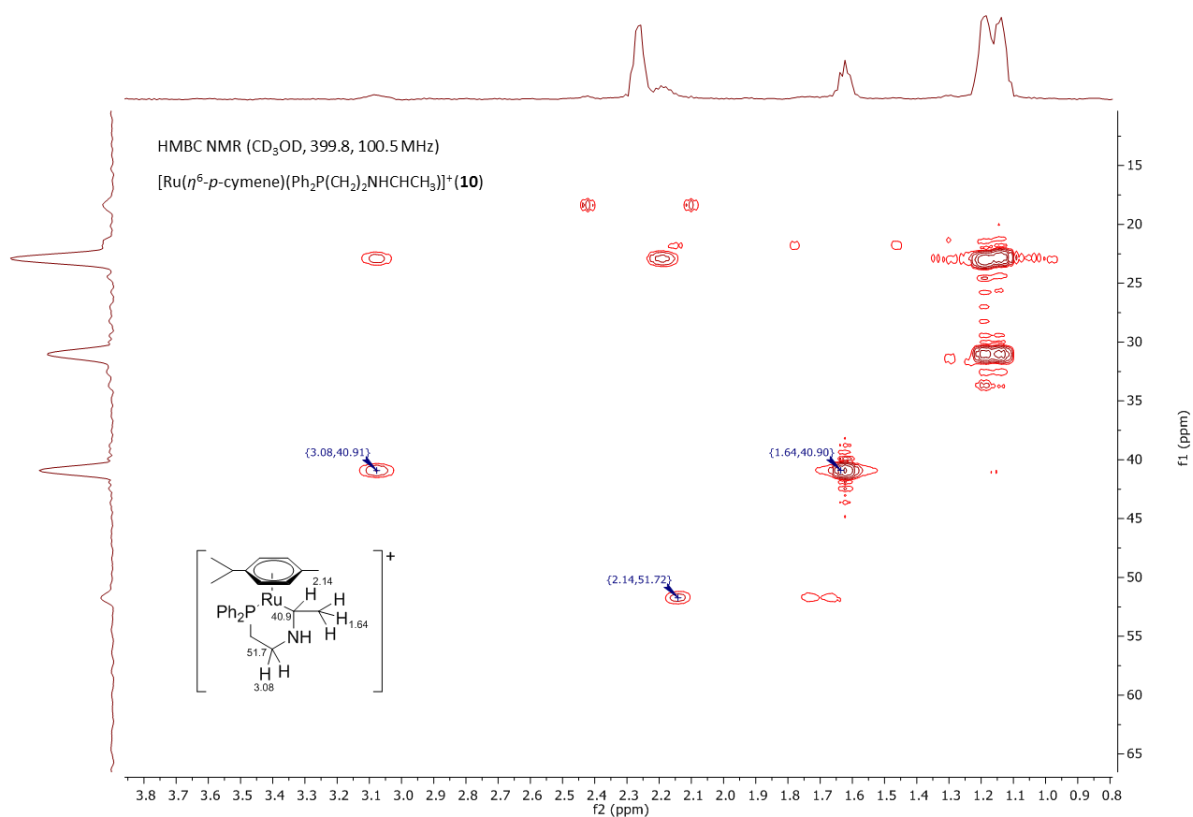
**Figure S27.** Edited HSQC NMR spectrum of [Ru( $\eta^6$ -*p*-cymene)(Ph<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NHCHCH<sub>3</sub>)]<sup>+</sup> (**10**) in methanol-*d*<sub>4</sub>, CH<sub>3</sub> and CH peaks in red, CH<sub>2</sub> and C<sub>q</sub> in blue



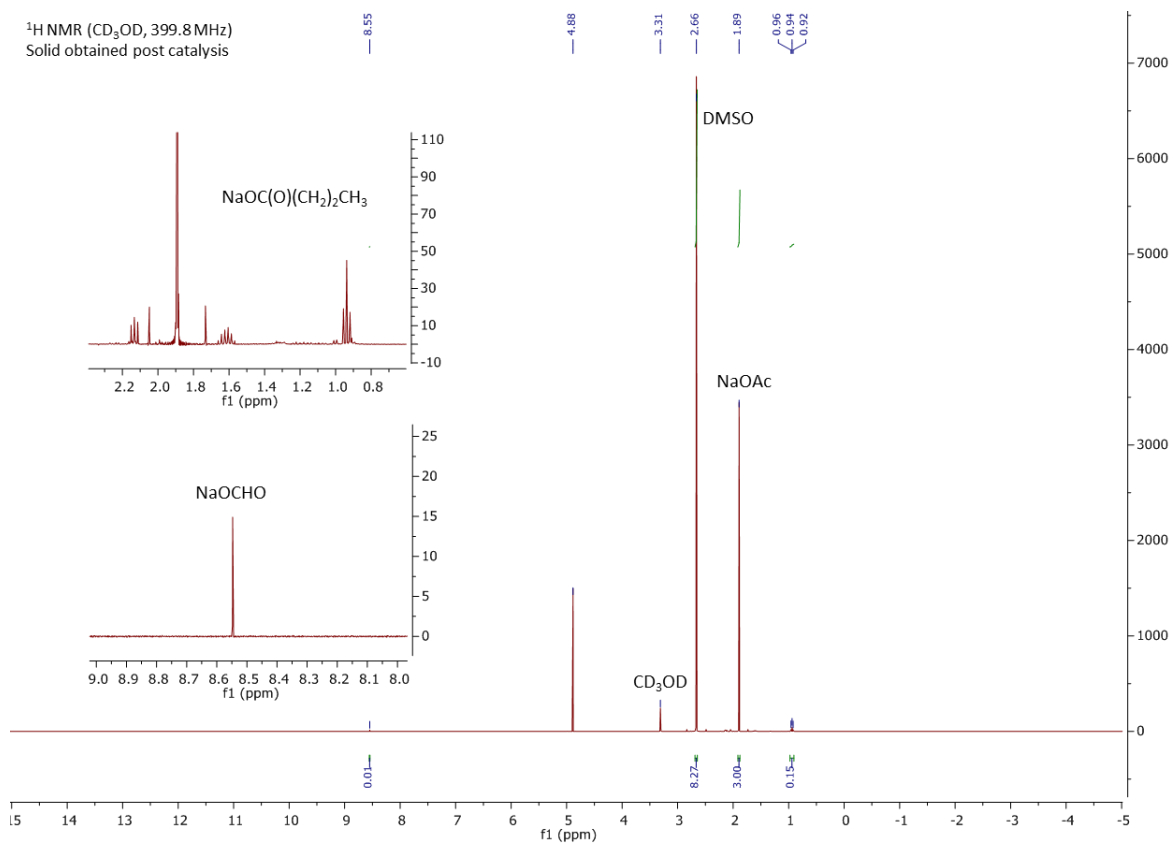
**Figure S28.** Edited HSQC NMR spectrum expansion of [Ru( $\eta^6$ -*p*-cymene)(Ph<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>NHCHCH<sub>3</sub>)]<sup>+</sup> (**10**) in methanol-*d*<sub>4</sub>, CH<sub>3</sub> and CH peaks in red, CH<sub>2</sub> and C<sub>q</sub> in blue



**Figure S29.** HMBC NMR spectrum of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2(\text{CH}_2)_2\text{NHCHCH}_3)]^+$  (**10**) in methanol- $d_4$



**Figure S30.** HMBC NMR spectrum expansion of  $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{Ph}_2(\text{CH}_2)_2\text{NHCHCH}_3)]^+$  (**10**) in methanol- $d_4$



**Figure S31.** <sup>1</sup>H NMR spectrum of solid obtained from run 1 with dmso added as a standard in methanol-*d*<sub>4</sub>

## References

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