Supporting Information for (Hexamethylbenzene)Ru Catalysts for the Aldehyde-Water Shift Reaction

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Experimental Details

All catalytic AWS experiments were prepared in a nitrogen-filled glovebox and carried out in 20 mL scintillation vials fitted with a pressure relief cap unless otherwise specified (Chemglass product number: CG-4912-05, 150 psig relief pressure). Aldehyde substrates were purchased from Sigma-Aldrich or Ark Pharm, Inc (for 2-hydroxymethylfurfural) and stored in a nitrogen-filled glovebox to prevent oxidation by air. H_2O (HPLC Grade) was purchased from Fischer Chemical and was sparged with N_2 or Ar. 1,4-dioxane (ACS Grade, unstabilized) was purchased from Fischer Chemical in small quantities and used quickly or sparged with N_2 or Ar and brought into a nitrogen-filled glovebox to prevent peroxide formation. Benzaldehyde, pivaldehyde, and furfural were distilled, degassed by freeze, pump, thaw cycles (3x), and stored in an N_2 filled glovebox. All other substrates were used as received. All data points from catalysis reported with a standard deviation were repeated in triplicate or greater. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance III 700 MHz, NEO 600 MHz equipped with Prodigy probe, Avance III 500 MHz, or Avance II 400 MHz spectrometers and referenced to the residual solvent peak.[1] All NMR spectra were recorded at ambient probe temperatures. Gas chromatography analysis is detailed below. Nominal mass accuracy ESI-MS data were obtained by use of a Waters Acquity UPLC system equipped with a Waters TUV detector (254 nm) and a Waters SQD single quadrupole mass analyzer with electrospray ionization. Samples were taken up in a suitable solvent introduced via loop injection (0.1% v/v formic acid aqueous carrier). Accurate mass measurement analyses were conducted on a Waters LCT Premier XE, time-of-flight, LCMS with electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of leucine enkephalin. Waters software calibrates the instruments, and reports measurements, by use of neutral atomic masses.

The following complexes were synthesized according to literature procedures: $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (**3**),[2] $[(\eta^6\text{-}C_6Me_6)Ru(o\text{-PDA})Cl]Cl$ (**4**),[3] $[(\eta^6\text{-}C_6Me_6)Ru(2,2'\text{-bipyridine})Cl]Cl$ (**5**),[4] $[(\eta^6\text{-}C_6Me_6)Ru(4,4'\text{-dimethoxy-}2,2'\text{-bipyridine})Cl]Cl$ (**6**),[5] and $[(\eta^6\text{-}C_6Me_6)Ru(6,6'\text{-dihydroxy-}2,2'\text{-bipyridine})Cl]Cl$ (**8**).[6] Using AgOTf, $[(\eta^6\text{-}C_6Me_6)Ru(4,4'\text{-dimethoxy-}2,2'\text{-bipyridine})OTf]OTf$ (**7**) was prepared in the manner of Ogo and Fukuzumi.[7] We thank the group of Professor Robert Crabtree (Yale University) for gift of 2-(2'-pyridyl)-2-propanol. **Caution, care should be taken when heating closed vessels, especially when gas is evolved throughout the reaction. For these catalysis experiments, Chemglass scintillation vials with PTFE pressure relief caps (CG-4912-05, rated to 150 psig) were used and reactions were run in a fume hood behind a blast shield.**

Procedure for Oxidation of Acetaldehyde

Chemglass brand 20 mL vials (CG-4912-05) were each charged with 0.005 mmol dimeric precatalyst or 0.010 mmol of monomeric precatalyst in air. The vials were brought into a N_2 filled glovebox, where a stirbar, 5 mL H_2O, and 2.5 mmol acetaldehyde were added. Vials were then sealed with PTFE pressure-relief caps and placed in an aluminum heating block on a preheated hotplate (95 °C) fitted with a programmable thermocouple probe (IKA brand ETS-D5). After the specified reaction time, vials were quickly cooled using ice. Previous studies in our group have shown that reactions run in 20 mL vials with pressure relief caps gave comparable results to those run in Teflon-sealed Schlenk tubes.[8] Product mixtures were analyzed by ^{1}H NMR (d1 = 30 s, aq = 3.5 s) by combining a 250 µL aliquot of reaction mixture and 250 µL of a 0.25 M phenol in D_2O solution as an internal standard. Acid selectivity is calculated by (%Acid Yield)/(%Acid Yield + %Alcohol Yield). Remaining starting material is the sum of acetaldehyde and the corresponding *gem*-diol, 1,1-ethanediol, formed in water. Chemicals shifts of products and reactants are given below.

^{1}H NMR Chemical Shifts for Peaks Used in Quantitation of Products of Acetaldehyde Reactions

All chemical shifts are reported in D_2O and standardized to residual D_2O at δ 4.79. If reaction was run in a mixed solvent containing 1,4-dioxane, chemical shifts referenced to 1,4-dioxane signal (3.75 ppm).[1]

Ethanol: δ 1.21 (t, $^3J_{HH}$ = 7.1 Hz, 3 H)
1,1-Ethanediol: δ 1.36 (d, $^3J_{HH}$ = 5.2 Hz, 3 H)
Acetic Acid: δ 2.10 (s, 3 H)
Acetaldehyde: δ 2.24 (d, $^3J_{HH}$ = 3.0 Hz, 3 H)
Phenol (Used as internal standard): δ 6.85-7.35

Procedure for Oxidation of Isobutyraldehyde, Pivaldehyde, Benzaldehyde, Furfural, HMF, and Cinnamaldehyde

Chemglass brand 20 mL vials (CG-4912-05) were charged with 0.005 mmol dimeric precatalyst or 0.010 mmol of monomeric precatalyst in air. The vials were brought into a N_2 filled glovebox, where a stirbar, 5 mL of the specified H_2O:1,4-dioxane mixture, and 2.5 mmol aldehyde were added. Vials were then sealed with PTFE pressure-relief caps and placed in an aluminum heating block on a preheated hotplate (95 °C) fitted with a programmable thermocouple probe (IKA brand ETS-D5). After the specified reaction time, vials were quickly cooled to room temperature using ice. The reaction mixture was diluted with 5 mL additional 1,4-dioxane to yield a homogeneous solution, and 400 µL was transferred to a 5 mL volumetric flask along with *n*-butyl alcohol or 1-hexanol as an internal standard. The volumetric flask was filled to 5 mL with 1,4-dioxane and analyzed by GC-FID. Reactions with HMF were characterized by quantitative

$^{13}C\{^{1}H\}$ NMR using an inverse-gated pulse sequence. All analytes were calibrated with reference to the internal standard using pure materials obtained from commercial sources. Acid selectivity is calculated by (%Acid Yield)/(%Acid Yield + %Alcohol Yield).

Procedure for Hydrogen Pressure Release Studies

Reaction vials were charged with **3** (0.005 mmol) in air. The closed system reactions were prepared in Chemglass brand 20 mL vials (CG-4912-05) as usual in a nitrogen filled glovebox. To inhibit solvent and substrate loss due to evaporation, taller, Chemglass brand 40 mL vials (CG-4912-06) were used for the vented reactions. Small, 25G needles were attached to oil bubblers using Luer lock adapters and tubing. Needles and tubing were thoroughly purged with N_2 prior to piercing the septa of reaction vials to prevent introduction of air. The vented and closed reactions were run side-by-side on the same hotplate as demonstrated in Figure S1. Note: temperature displayed on ETS-D5 thermocouple in Figure S1 is below 85 °C, as picture was taken immediately after placing room temperature vials on the preheated hotplate.

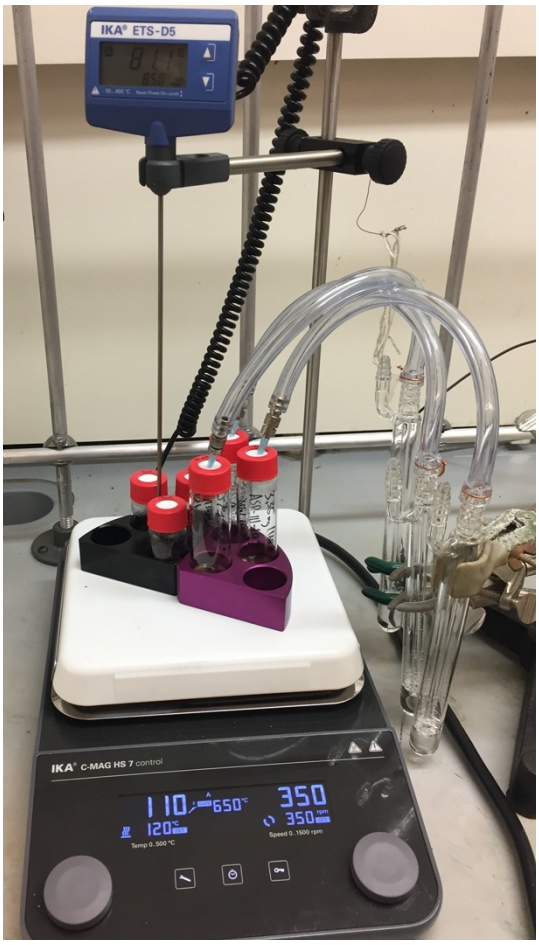


Figure S1. Reaction setup for side by side vented (right) and closed (left) reactions studying the effect of H_2 pressure release.

Method and Analyte Retention Times for GC-FID Analysis of Catalytic Reactions

Instruments: Agilent Technologies 7890A or 7890-B Gas Chromatography System, FID Detector

Column: Agilent Technologies DB-FFAP (Part Number: 122-3232)

Method:

Inlet: Split, 50:1 ratio

Inlet temperature: 280 °C

Detector temperature: 280 °C

Pivaldehyde, Benzaldehyde, Furfural Reactions

Oven temperature control: 40 °C starting temperature, held for 4 min. Temperature is then ramped at 30 °C/min to 230 °C and held at 230 °C for 3 minutes.

Isobutyraldehyde Reactions

Oven temperature control: 40 °C starting temperature, held for 4 min. Temperature is then ramped at 20 °C/min to 200 °C and held at 200 °C for 3 minutes.

Cinnamaldehyde Reactions

Oven temperature control: 40 °C starting temperature, held for 4 min. Temperature is then ramped at 30 °C/min to 180 °C before ramping at 15 °C/min to 235 °C and held at 235 °C for 13 minutes.

Retention times (min):

1,4-dioxane – 2.92

n-butyl alcohol (internal standard) – 4.54

1-hexanol (internal standard) – 7.51

Isobutyraldehyde – 1.29

2,2-dimethylpropanol – 4.32

Isobutyric acid – 9.05

Pivaldehyde – 1.26

Neopentyl alcohol – 4.61

Pivalic acid – 9.11

Benzaldehyde – 7.63

Benzyl alcohol – 9.5

Benzoic acid – 11.47

Furfural – 6.34

Furfuryl alcohol – 7.26

2-Furoic acid – 10.24

3-phenylpropanal – 8.81

trans-cinnamaldehyde – 9.89

3-phenyl 1-propanol – 9.84

trans-cinnamyl alcohol – 10.93

3-phenyl propionic acid – 12.51

trans-cinnamic acid – 14.01

Reaction of [(η^6-C_6Me_6)Ru(*o*-PDA)Cl)[Cl] with Benzaldehyde

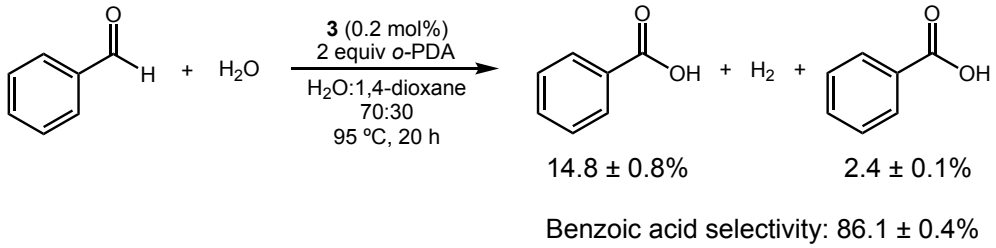


Figure S2. Oxidation of benzaldehyde with **3** and addition of *o*-PDA.

Because **3** and **4** performed similarly under acetaldehyde screening conditions, both were tested for reactivity with benzaldehyde. Previous reactions found that stirring **3** and 2 equiv. *o*-PDA for 15 minutes in water before addition of substrate or heating resulted in a color change consistent with formation of **4**. *in situ* Formed **4** was found to give comparable yields and selectivities as independently-prepared **4**. When *in situ* prepared **4** was used for the oxidation of benzaldehyde, greater benzoic acid selectivity (86.1%) compared to **3** (80.3%) was observed. In addition, conversion of benzaldehyde with **4** (17.2%) was significantly lower than that of **3** (32.8%).

Detection of H_2 in Reaction Headspace

Procedure: Standard reaction conditions for acetaldehyde oxidation were used and the vial was cooled on ice prior to gas sampling. Using a Hamilton Gas Tight syringe with sampling valve, the vial septum was punctured and a 50 µL aliquot was taken and injected into the GC-TCD. Comparison to known gas samples confirmed identity of H_2 in the reaction headspace. Figure S3 shows an overlay of GC-TCD chromatographs of an air sample, H_2 sample, and reaction headspace sample (each 50 µL injections). The gases H_2 and N_2 can clearly be seen in the reaction headspace sample.

Instrument: Agilent Technologies 7890-B Gas Chromatography System
Detector: Thermal Conductivity Detector (TCD) (Negative Polarity Mode)
Column: Mol-Sieve 5 Å 6-ft packed column (Agilent Part Number: G3591-80017)
Method:

Oven temperature: 30 °C (constant)
Inlet: Agilent Ar/Methane setting
Carrier gas: Argon
Inlet flow rate: 43 mL/min
Septum purge flow: 3 mL/min
Column flow rate: 40 mL/min
TCD Detector Temp: 225 °C
Detector Reference Flow: 50 mL/min
Detector Makeup Flow: 3 mL/min

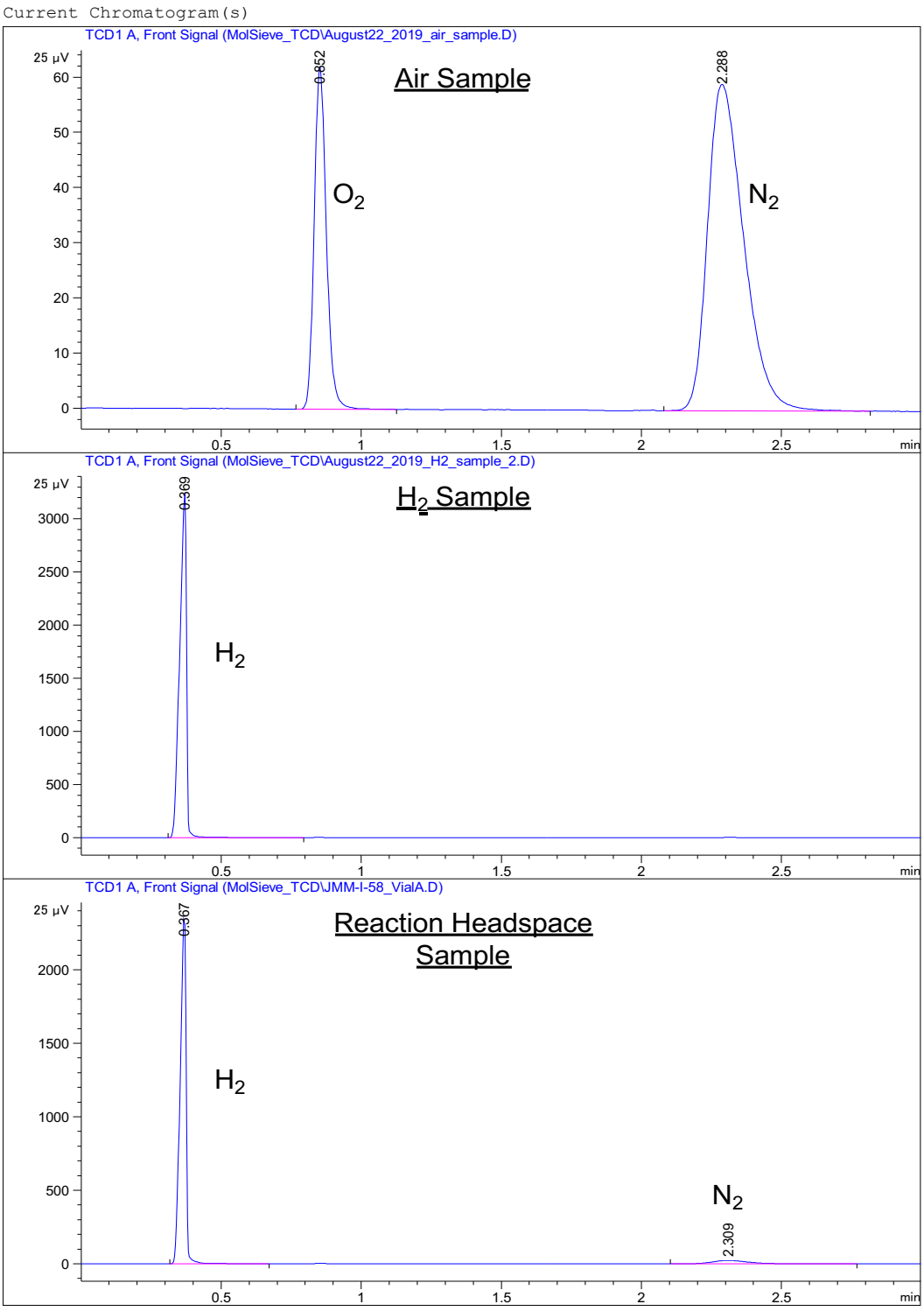


Figure S3. Overlay of GC-TCD chromatographs from air sample (top), authentic H_2 sample (middle), and reaction headspace gas sample (bottom). Reaction was performed under standard screening conditions for 5 h at 95 °C in H_2O (5 mL) with acetaldehyde substrate (2.5 mmol) and **3** as precatalyst (0.2 mol%).

Synthesis of ((η^6-C_6Me_6)Ru(4,4'-dimethoxy-2,2'-bipyridine)OTf)[OTf] (7).

((η^6-C_6Me_6)Ru(4,4'-dimethoxy-2,2'-bipyridine)OTf)[OTf] (**7**) was prepared by the same method used for the SO_4^{2-} analogue, using AgOTf instead of Ag_2SO_4.[7, 9] The product was recrystallized from H_2O and the ^{1}H NMR chemical shifts match (within 0.01 ppm) those reported for [(η^6-C_6Me_6)Ru(4,4'-dimethoxy-2,2'-bipyridine)]$^{2+}$.[7, 10] ^{1}H NMR (400 MHz, D_2O) δ 2.11 (s, 18H), 4.07 (s, 6H), 7.40 (dd, $^3J_{HH}$ = 6.6 Hz, $^4J_{HH}$ = 2.7 Hz, 2H), 7.85 (d, $^4J_{HH}$ = 2.7 Hz, 2H), 8.90 (d, $^3J_{HH}$ = 6.6 Hz, 2H). ^{19}F{^{1}H} NMR (376 MHz, D_2O) δ -78.79, ^{13}C{^{1}H} NMR (151 MHz, D_2O) δ 15.4 (s), 57.3 (s), 95.5 (s), 111.1 (s), 114,8 (s), 120.2 (q, $^1J_{CF}$ = 316.7 Hz), 154.6 (s), 157.3 (s), 169.5 (s). Nominal mass ESI-MS m/z = 629.5 $[M]^+$ (76%), 240.2 $[M\text{-}OTf]^{2+}$(100%). Accurate Mass Measurement (ESI+, TOF) $C_{25}H_{30}F_3N_2O_5RuS$: Theoretical Mass: 629.0871, Observed Mass: 629.0877.

Characterization of ((η^6-C_6Me_6)Ru(4,4'-dimethoxy-2,2'-bipyridine)OTf)[OTf] (7).

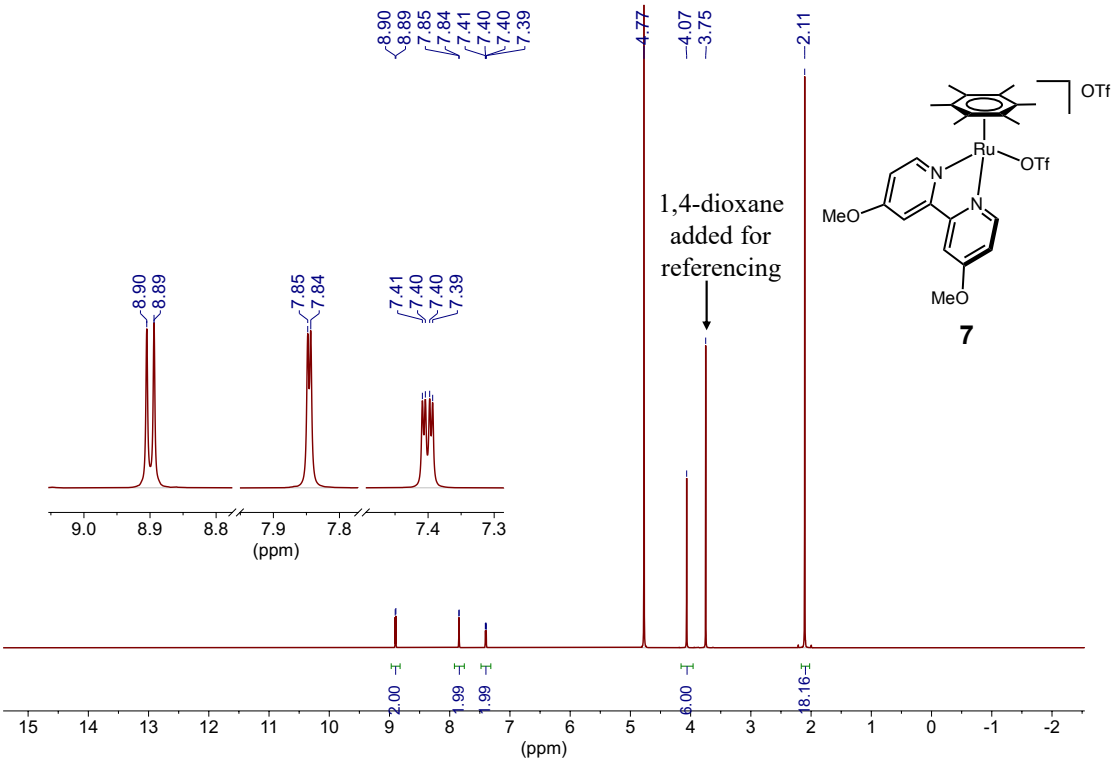


Figure S4. ^{1}H NMR (600 MHz, D_2O) of [(η^6-C_6Me_6)Ru(4,4'-dimethoxy-2,2'-bipyridine)OTf][OTf] (**7**). 1,4-dioxane added for referencing (3.75 ppm).[1]

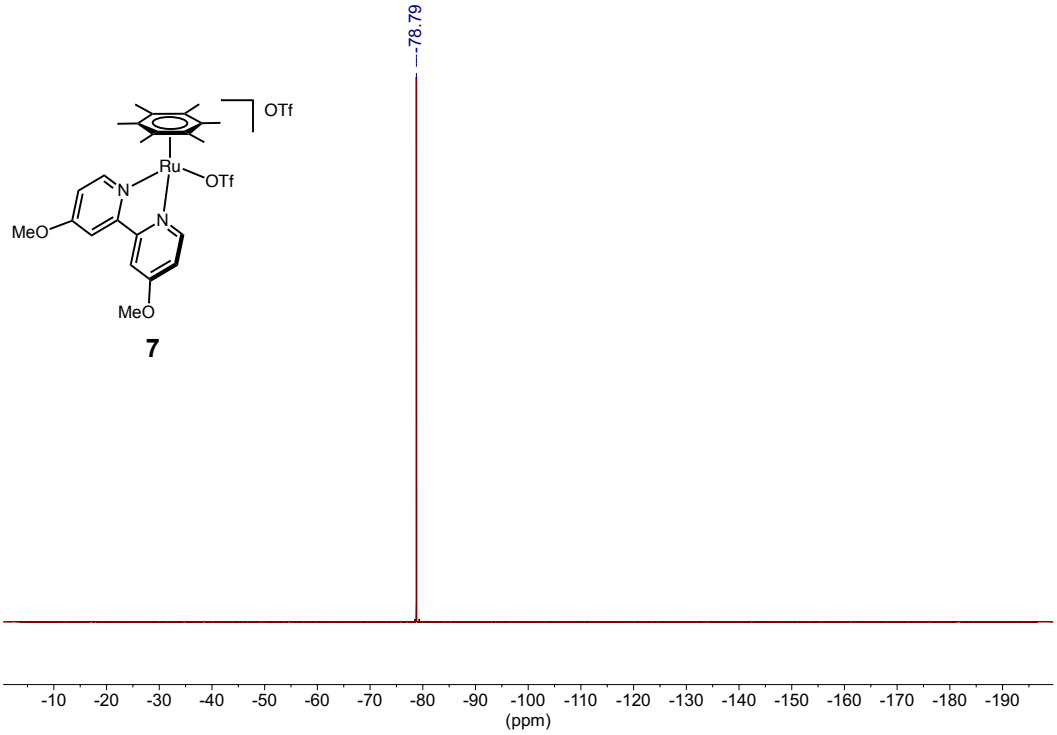


Figure S5. $^{19}F\{^{1}H\}$ NMR (376 MHz, D_2O) of [(η^6-C_6Me_6)Ru(4,4'-dimethoxy-2,2'-bipyridine)OTf][OTf] (**7**).

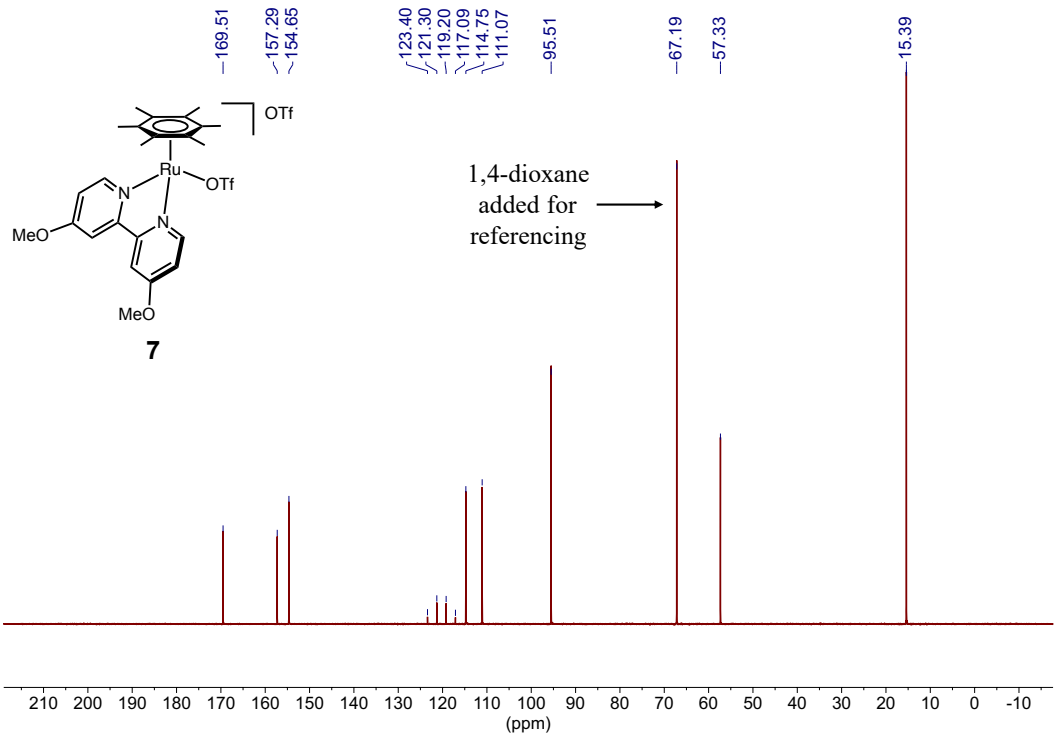


Figure S6. $^{13}C\{^{1}H\}$ NMR (151 MHz, D_2O) of [(η^6-C_6Me_6)Ru(4,4'-dimethoxy-2,2'-bipyridine)OTf][OTf] (**7**).

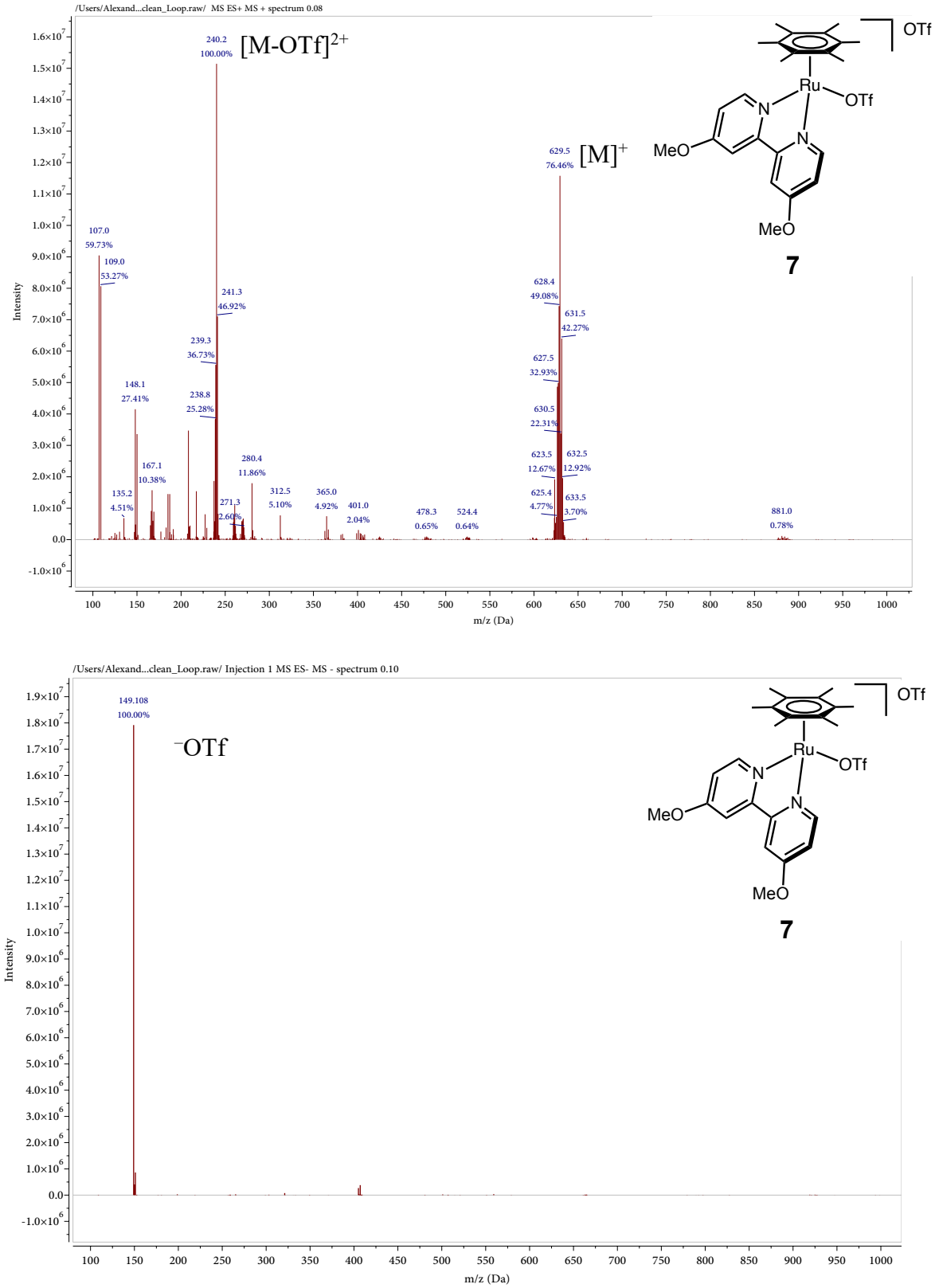


Figure S7. Nominal mass ESI-MS spectra of ((η^6-C_6Me_6)Ru(4,4'-dimethoxy-2,2'-bipyridine)OTf)[OTf] (**7**). Loop injection of sample taken up in H_2O, H_2O carrier with 0.1% formic acid. **Top**: Positive mode, **Bottom**: Negative mode.

Synthesis of ((η^6-C_6Me_6)Ru((2-(2′-pyridyl)-2-propanoate)Cl (9).

In an N_2 filled glovebox, a Teflon stoppered Schlenk tube was loaded with [(η^6-C_6Me_6)$RuCl_2$]$_2$ (**3**) (80.7 mg, 0.121 mmol, (2-(2′-pyridyl)-2-propanol (32.9 mg, 0.240 mmol, 1.99 equiv), $NaHCO_3$ (88.0 mg, 1.05 mmol, 8.7 equiv), and a Teflon-coated stirbar. Dry, degassed methanol (20 mL) and acetone (12 mL) were then added. The Schlenk tube was then sealed, brought out of glovebox, and heated to 50 °C for 55 hours, yielding a dark red solution. Upon cooling to room temperature, the reaction solution was filtered in air to remove undissolved $NaHCO_3$, and the solvent was removed *in vacuo*. In N_2 filled glovebox, the crude red product was dissolved in minimal Et_2O, filtered through amorphous silica, and placed in a -30 °C freezer. After several days, red crystalline needles were harvested, rinsed with cold pentane, and dried under high vacuum. Yield: 50.6 mg (49%). Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of a MeOH solution of **9**. X-ray crystallography data for **9** can be found via the Cambridge Crystallographic Data Centre under CCDC 2034882.

^{1}H NMR (500 MHz, acetone-d_6) δ 1.30 (s, 3H), 1.33 (s, 3H), 2.03 (s, 18H), 7.07 (dt, J^3_{HH} = 8.0 Hz, J^4_{HH} = 1.0 Hz, 1H), 7.29 (ddd, J = 7.3, 5.7, 1.5 Hz, 1H), 7.70 (td, J = 7.6, 1.6 Hz, 1H), 8.67 (ddd, J = 5.5, 1.6, 0.8 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, Acetone-d_6) δ 15.31 (s, $C_6(CH_3)_6$), 34.46 (s, CCH_3), 35.97, (s, CCH_3), 83.70 (s), 90.84 (s, $C_6(CH_3)_6$), 121.57 (s), 123.51 (s), 137.57 (s), 150.90 (s), 180.05 (s). ESI-MS m/z = 400.4 ([M-Cl]$^+$). Accurate Mass Measurement (ESI+, TOF) $C_{20}H_{24}ClNORu$: Theoretical Mass: 436.0981, Observed Mass: 436.0969

Crystal Structure of ((η^6-C_6Me_6)Ru((2-(2′-pyridyl)-2-propanoate)Cl (9).

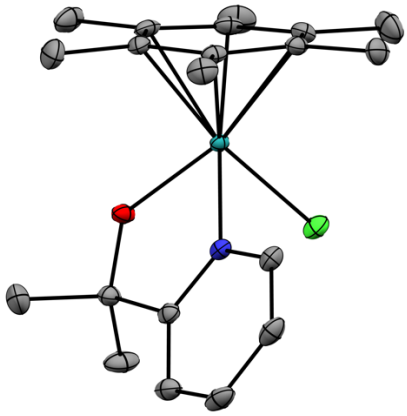


Figure S8. Molecular structure of ((η^6-C_6Me_6)Ru((2-(2′-pyridyl)-2-propanoate)Cl (**9**) as determined by single crystal X-ray diffraction. Hydrogen atoms and co-crystallized methanol molecule omitted for clarity. Thermal ellipsoids: 50% probability.

Table S1. Summary of Structure Determination of ((η^6-C_6Me_6)Ru((2-(2′-pyridyl)-2-propanoate)Cl (9)

CCDC Number	2034882
Empirical formula	$C_{21}H_{32}NO_2ClRu$
Formula weight	466.99

Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a	14.7118(6)Å
b	9.3818(4)Å
c	14.7793(7)Å
β	91.266(2)°
γ	90°
Volume	2039.39(15)$Å^3$
Z	4
d_{calc}	1.521 g/cm^3
μ	0.915 mm^{-1}
F(000)	968.0
Crystal size, mm	0.31 × 0.25 × 0.12
2θ range for data collection	3.864 - 55.048°
Index ranges	$-19 \leq h \leq 19$, $-12 \leq k \leq 12$, $-19 \leq l \leq 19$
Reflections collected	50442
Independent reflections	4688[R(int) = 0.0218]
Data/restraints/parameters	4688/0/245
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	$R_1 = 0.0161$, $wR_2 = 0.0418$
Final R indexes [all data]	$R_1 = 0.0168$, $wR_2 = 0.0423$
Largest diff. peak/hole	0.41/-0.36 $eÅ^{-3}$

NMR Characterization of ((η^6-C_6Me_6)Ru((2-(2′-pyridyl)-2-propanoate)Cl (9).

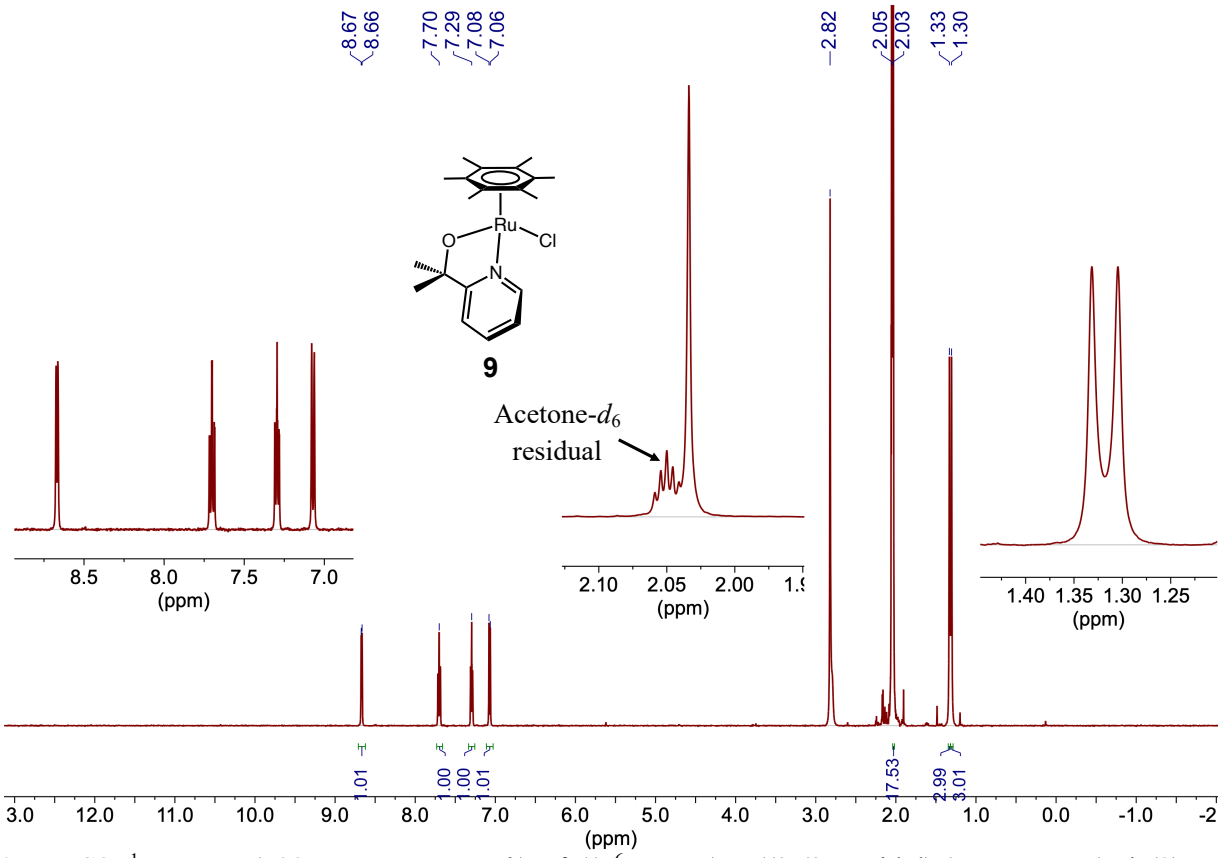


Figure S9. ^{1}H NMR (500 MHz, acetone-d_6) of ((η^6-C_6Me_6)Ru((2-(2′-pyridyl)-2-propanoate)Cl (**9**). Note: C_6Me_6 of complex and residual acetone-d_6 signal overlap slightly. Due to disparate signal intensity, signals were magnified (insets), bound C_6Me_6 peak extends past the top of the image.

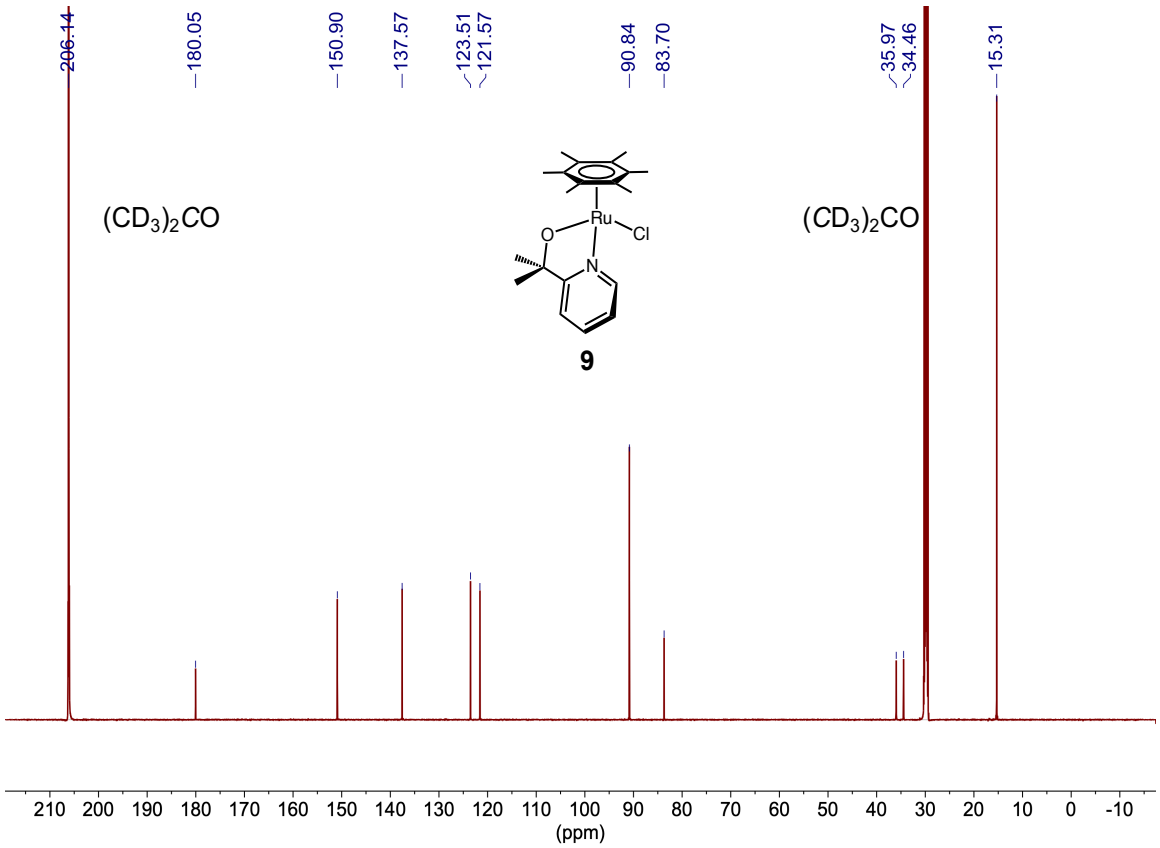
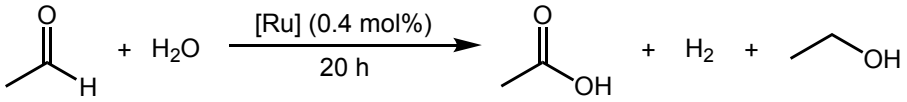


Figure S10. $^{13}C\{^{1}H\}$ NMR (151 MHz, acetone-d_6) of ((η^6-C_6Me_6)Ru((2-(2′-pyridyl)-2-propanoate)Cl

Temperature Dependence of Selectivity

In early screens with acetaldehyde as substrate, it was noted that selectivity for acetic acid did not change greatly with the reaction temperature used. Using **4**, formed *in situ* by stirring **3** and 2 equiv. *o*-PDA, reactions were run at 70, 80, and 105 °C in both 100% H_2O (Figure S11) and 50:50 H_2O:1,4-dioxane (Figure S12). In H_2O, average acetic acid selectivity is 95.7, 94.7, and 94.8% at 70, 80, and 105 °C, respectively. In 50:50 H_2O:1,4-dioxane, average acetic acid selectivity is 93.1, 91.6, and 94.8% at 70, 80, and 105 °C, respectively.



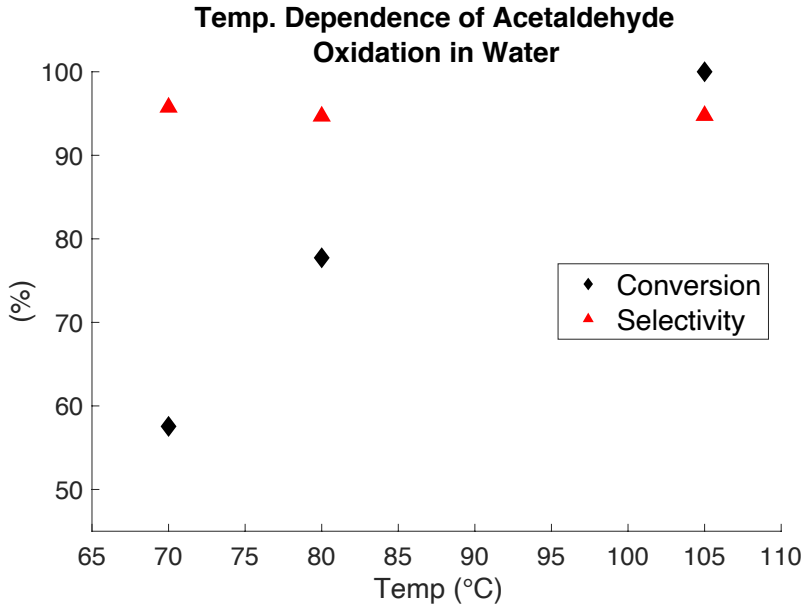


Figure S11. Temperature dependence of acetaldehyde oxidation by **4** in H_2O for 20 h. Reaction conditions: 5 mL H_2O, 2.5 mmol acetaldehyde, 0.2 mol% **3**, 0.4 mol% *o*-PDA. Quantified by ^{1}H NMR using phenol internal standard. Complex **3** and *o*-PDA stirred 15 minutes to form **4** in situ before substrate addition.

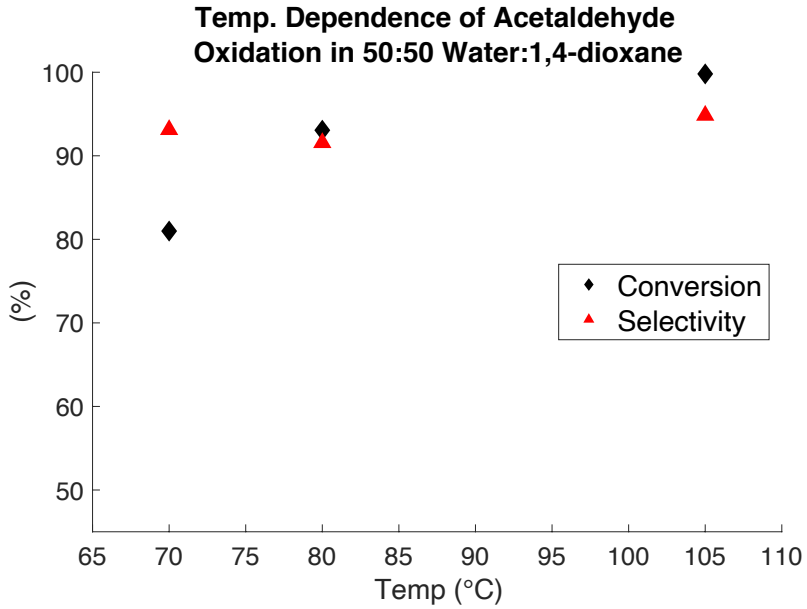
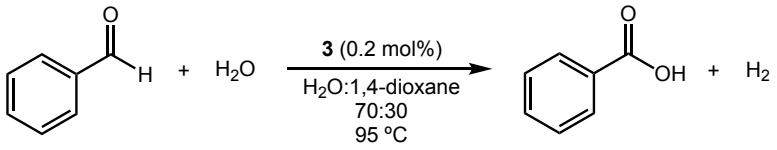


Figure S12. Temperature dependence of acetaldehyde oxidation by **4** in 50:50 H_2O:1,4-dioxane for 20 h. Reaction conditions: 2.5 mL H_2O, 2.5 mL 1,4-dioxane, 2.5 mmol acetaldehyde, 0.2 mol% **3**, 0.4 mol% *o*-PDA. Quantified by ^{1}H NMR using phenol internal standard. Complex **3** and *o*-PDA stirred 15 minutes to form **4** in situ before substrate addition.

Reaction Profile for Benzaldehyde Oxidation Data

Full data for time course studies of benzaldehyde oxidation, as discussed in main text. Initial catalysis gives high benzoic acid selectivity of 87%, before dropping off (Table S2). Between 20 and 40 hours, additional substrate consumed is almost entirely through aldehyde disproportionation, which forms equimolar alcohol and acid products.

Table S2. Effect of time on benzaldehyde reaction profile.

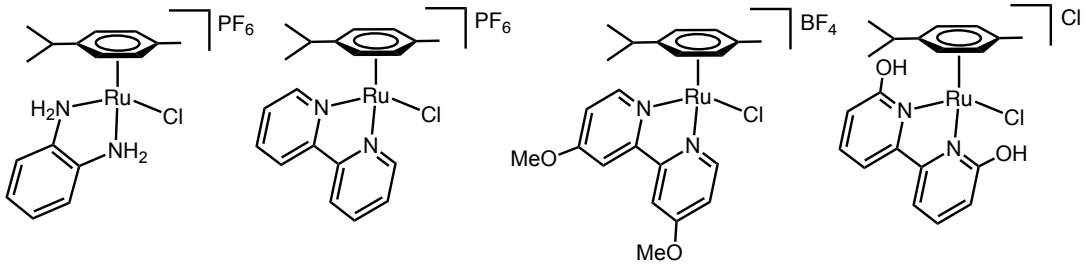


Time (h)	Benzoic Acid Yield (%)	Benzyl Alcohol Yield (%)	Overall Selectivity (%)	Selectivity Since Previous Time Point (%)
5	13.8(9)	2.0(3)	87.3(8)	87.3
20	26.3(5)	6.5(2)	80.3(3)	73.5
40	35.8(2)	13.7(4)	72.3(6)	56.9

Reaction conditions: 3.5 mL H_2O, 1.5 mL 1,4-dioxane, 2.5 mmol benzaldehyde, 0.005 mmol **3** (0.2 mol%), 95 °C. Quantified by GC-FID. All entries repeated in triplicate and standard deviations are given in parentheses.

Comparison of Ru–N bond distances in analogous (*p*-cymene)Ru complexes

While some of the [(η^6-C_6Me_6)Ru complexes tested for catalysis have not been crystallographically characterized, their *p*-cymene derivatives have (Figure S13). It is evident that the Ru–N bonds are significantly elongated with primary amine donors compared to bipyridine ligands with tertiary amine donors. We propose that elongated Ru–N bonds with *o*-PDA result in greater hemilability, opening up a coordination site so that beta-hydride elimination can occur.



Ru–N distance (Å)	2.141(2) 2.156(2)	2.079 2.087	2.084(3) 2.086(3)	2.1162(12) 2.1253(12)
Ru–Cl distance (Å)	2.4039(8)	2.401	2.410(1)	2.3899(4)
Reference:	Sadler[3]	Xiao[11]	Espino[12]	Papish[6]

Figure S13. Single crystal X-ray structures of relevant (η^6-*p*-cymene)Ru complexes with selected bond lengths shown. Standard deviation in parentheses.

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